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Form PTO-1390
(REV 10-95)

U. S. Department of Commerce Patent and Trademark Office

ATTORNEY'S DOCKET NUMBER

HP/5-22037A/PCT

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

10/018199

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

INTERNATIONAL APPLICATION NO.

PCT/EP 00/05314

INTERNATIONAL FILING DATE

June 8, 2000

PRIORITY DATE CLAIMED

June 18, 1999

TITLE OF INVENTION

Micropigment mixture

APPLICANT(S) FOR DO/EO/US

Helmut Luther

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
- a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
- b. ☒ has been transmitted by the International Bureau. (See attached Form PCT/IB/308)
- c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English 35 U.S.C. 371(c)(2).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
- a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
- b. ☐ have been transmitted by the International Bureau.
- c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
- d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included.

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ **A FIRST preliminary amendment.**
- ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information: (See attached Form PCT/ISA/210)

U.S. APPLICATION NO. (if known, see 37 CFR 1.51) 10/018199		INTERNATIONAL APPLICATION NO. PCT/EP 00/05314		ATTORNEY'S DOCKET NUMBER HP/S-22037/A/PCT	
17. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492(a) (1)-(5)):				CALCULATIONS PTO USE ONLY	
Search Report has been prepared by the EPO or JPO				\$890.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482)				\$710.00	
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))				\$740.00	
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO				\$1040.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)				\$100.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$890.00	
Surcharge of \$130.00 for furnishing the oath of declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
CLAIMS		NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	27	- 20 =	7	X \$18.00	\$126.00
Independent claims	1	- 3 =	0	X \$84.00	\$
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$280.00	\$
TOTAL OF ABOVE CALCULATIONS =				\$1,016.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL =				\$1,016.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$1,016.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				+	
TOTAL FEES ENCLOSED =				\$	
				Amount to be refunded	\$
				charged	\$1,016.00
a. <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed.					
b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. 03-1935 in the amount of \$1,016.00 to cover the above fees. A duplicate copy of this sheet is enclosed.					
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 03-1935. A duplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
PLEASE ASSOCIATE THE ATTACHED APPLICATION WITH CUSTOMER NUMBER 000324 AND SEND ALL CORRESPONDENCE TO: JoAnn Villamizar, Ciba Specialty Chemicals Corporation Patent Department 540 White Plains Road P.O. Box 2005 Tarrytown, NY 10591-9005 Date: DEC 14 2001					
				<i>Kevin T. Mansfield</i> SIGNATURE	
				Kevin T. Mansfield, Agent for Applicant NAME Reg. No. 31,635	

CASE HP/5-22037/A/PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE PCT NATIONAL STAGE APPLICATION OF
HELMUT LUTHER ET AL
INTERNATIONAL APPLICATION NO. PCT/EP 00/05314
FILED: JUNE 8, 2000
FOR: MICROPIGMENT MIXTURE
U.S. APPLICATION NO: UNASSIGNED
35 USC 371 DATE:

Group Art Unit: unassigned
Examiner: unassigned

Assistant Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir:

Kindly amend this application as follows prior to calculation of the filing fee and consideration on the merits.

IN THE CLAIMS

Please cancel claims 1-31.

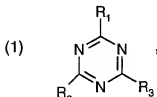
Please add the following claims.

--32. (new) A method of protecting human and animal skin and hair against the damaging effects of UV radiation by treating the skin or hair with a cosmetic formulation, comprising a mixture of micronised organic UV filters.

33. (new) A method according to claim 32, wherein the mixtures of organic UV filters are chosen from at least 2 classes of organic UV filters selected from the group consisting of: triazine derivatives, benzotriazole derivatives, amides containing a vinyl group, cinnamic acid derivatives, sulfonated

benzimidazoles, Fischer base derivatives, diphenylmalonic acid dinitriles, oxalyl amides, camphor derivatives, diphenyl acrylates, para-aminobenzoic acid (PABA) and derivatives thereof, salicylates and benzophenones.

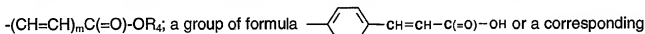
34. (new) A method according to claim 32, wherein the organic UV filters are chosen from triazine derivatives of formula



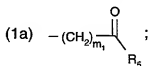
wherein

R_1 , R_2 and R_3 are each independently of the others hydrogen; OH; C_1 - C_{18} alkoxy; $-NH_2$; $-NH-R_4$; $-N(R_4)_2$; or $-OR_4$,

R_4 is C_1 - C_8 alkyl; phenyl; phenoxy; anilino; pyrrolo, wherein phenyl, phenoxy, anilino and pyrrolo are unsubstituted or may be substituted by one, two or three OH groups, carboxy, $-CO-NH_2$, C_1 - C_8 alkyl or C_1 - C_8 alkoxy; a methyldene-camphor group; a group of formula

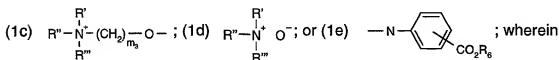
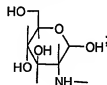


alkali metal, ammonium, mono-, di- or tri- C_1 - C_4 alkylammonium, mono-, di- or tri- C_2 - C_4 alkanolammonium salt, or a C_1 - C_8 alkyl ester thereof; or a radical of formula



R_5 is hydrogen; C_1 - C_8 alkyl which is unsubstituted or substituted by one or more OH groups;

C_1 - C_8 alkoxy; amino; mono- or di- C_1 - C_8 alkylamino; M; a radical of formula (1b)

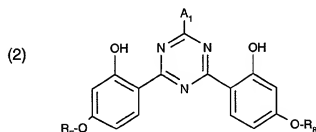


R' , R'' and R''' are each independently of the others C_1 - C_{14} alkyl which is unsubstituted or substituted by one or more OH groups;

R_6 is hydrogen; M; C_1 - C_8 alkyl; or a radical of formula $-(CH_2)_{m_2}O-T_1$;

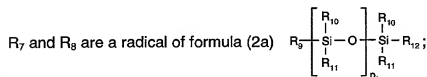
- M is a metal cation;
 T₁ is hydrogen; or C₁-C₈alkyl;
 m is 0 or 1;
 m₂ is from 1 to 4; and
 m₃ is from 2 to 14.

35. (new) A method according to claim 32, wherein the organic UV filters are chosen from triazine derivatives of formula



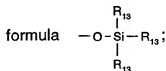
wherein

R₇ and R₈ are each independently of the other C₁-C₁₈alkyl; C₂-C₁₈alkenyl; a radical of formula -CH₂-CH(OH)-CH₂-O-T₁; or

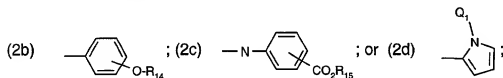


R₉ is a direct bond; a straight-chain or branched C₁-C₄alkylene radical or a radical of formula -C_{m₁}H_{2m₁}-O-;

R₁₀, R₁₁, and R₁₂ are each independently of the others C₁-C₁₈alkyl; C₁-C₁₈alkoxy or a radical of



R₁₃ is C₁-C₈alkyl;
 m₁ is from 1 to 4;
 p₁ is from 0 to 5;
 A₁ is a radical of formula



R₁₄ is hydrogen; C₁-C₁₀alkyl, $-(CH_2CHR_{16}-O)_{n_1}-R_{15}$; or a radical of formula $-CH_2-CH(-OH)-CH_2-O-T_1$;

R₁₅ is hydrogen; M; C₁-C₅alkyl; or a radical of formula $-(CH_2)_{m_2}-O-(CH_2)_{m_3}-T_1$;

R₁₆ is hydrogen; or methyl;

T₁ is hydrogen; or C₁-C₈alkyl;

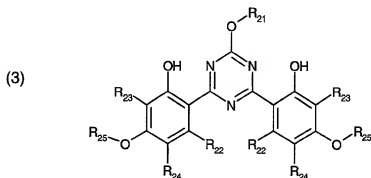
Q₁ is C₁-C₁₈alkyl;

M is a metal cation;

m₂ and m₃ are each independently of the other from 1 to 4; and

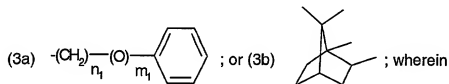
n₁ is from 1 to 16.

36. (new) A method according to claim 32, wherein the organic UV filters are chosen from triazine derivatives of formula



wherein

R₂₁ is C₁-C₃₀alkyl; C₂-C₃₀alkenyl; C₅-C₁₂cycloalkyl unsubstituted or mono- or poly-substituted by C₁-C₅alkyl; C₁-C₅alkoxy-C₁-C₁₂alkyl; amino-C₁-C₁₂alkyl; C₁-C₅monoalkylamino-C₁-C₁₂alkyl; C₁-C₅dialkylamino-C₁-C₁₂alkyl; a radical of formula



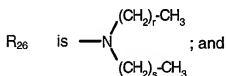
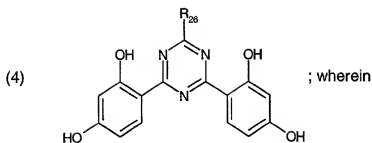
R₂₂, R₂₃ and R₂₄ are each independently of the others hydrogen, -OH; C₁-C₃₀alkyl, C₂-C₃₀alkenyl,

R₂₅ is hydrogen; or C₁-C₅alkyl;

m₁ is 0 or 1; and

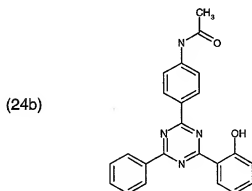
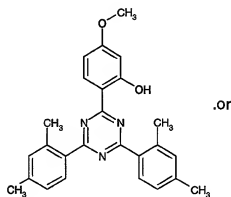
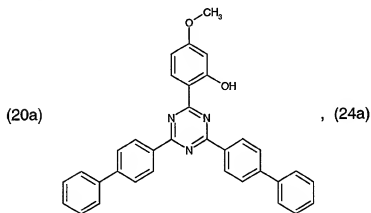
n₁ is from 1 to 5.

37. (new) A method according to claim 32, wherein the organic UV filters are chosen from triazine derivatives of formula

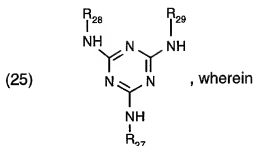


r and s are each independently of the other from 0 to 20.

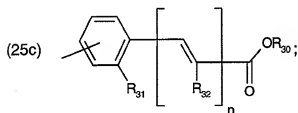
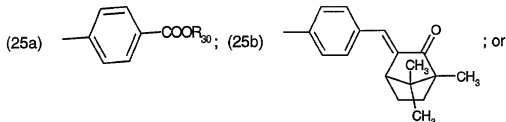
38. (new) A method according to claim 32, wherein the organic UV filters are chosen from triazine derivatives of formula



39. (new) A method according to claim 32, wherein the organic UV filters are chosen from triazine derivatives of formula



R₂₇, R₂₈ and R₂₉ are each independently of the others a radical of formula



R₃₀ is hydrogen; an alkali metal; or an ammonium group -N(R₃₃)₄.

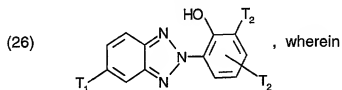
R₃₃ is hydrogen, C₁-C₅alkyl; or a polyoxyethylene radical that has from 1 to 10 ethylene oxide units and the terminal OH group is optionally etherified with a C₁-C₆alcohol;

R₃₁ is hydrogen; -OH; or C₁-C₆alkoxy;

R₃₂ is hydrogen or -COOR₃₀; and

n is 0 or 1.

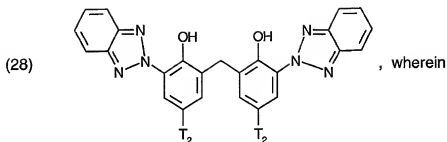
40. (new) A method according to claim 32, wherein the organic UV filters are chosen from benzotriazole derivatives of formula



T₁ is C₁-C₅alkyl or hydrogen; and

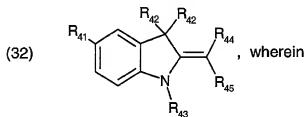
T₂ is C₁-C₅alkyl or phenyl-substituted C₁-C₅alkyl.

41. (new) A method according to claim 32, wherein the organic UV filters are chosen from benzotriazole derivatives of formula



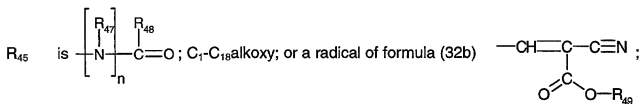
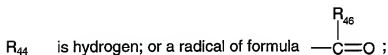
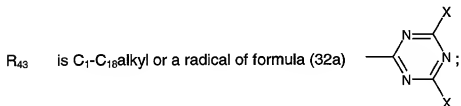
T_2 is C_1 - C_4 alkyl, isooctyl, or phenyl-substituted C_1 - C_5 alkyl.

42. (new) A method according to claim 32, wherein the Fischer base aldehydes correspond to formula



R_{41} is hydrogen; C_1 - C_6 alkyl; C_1 - C_{18} alkoxy; or halogen;

R_{42} is C_1 - C_6 alkyl; C_5 - C_7 cycloalkyl; or C_6 - C_{10} aryl;



R_{46} and R_{47} are each independently of the other hydrogen; or C_1 - C_5 alkyl;

R_{48} is hydrogen; C_1 - C_5 alkyl; C_5 - C_7 cycloalkyl; phenyl; phenyl- C_1 - C_3 alkyl;

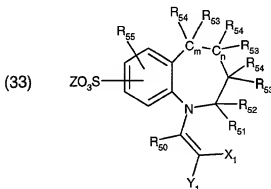
R_{49} is C_1 - C_{18} alkyl;

*Nc1ccc(cc1)C(=O)NR46

HO
—
—OH; and

is 0 or 1.

43. (new) A method according to claim 32, wherein the organic UV filters are chosen from compounds of formula



wherein

$R_{50}, R_{51}, R_{52}, R_{53}, R_{54}$ are each independently of the others hydrogen, C_1 - C_8 alkyl or C_5 - C_{10} cycloalkyl;
 R_{55} is hydrogen; C_1 - C_8 alkyl; C_5 - C_{10} cycloalkyl; hydroxyl; C_1 - C_8 alkoxy; $COOR_{56}$; or $CONR_{57}R_{58}$;
 R_{56}, R_{57} and R_{58} are each independently of the others hydrogen or C_1 - C_8 alkyl;
 X and Y are each independently of the other hydrogen, $-CN$; CO_2R_{59} ; $CONR_{59}R_{60}$; or COR_{59} ;

it being possible for the radicals X and Y additionally to be a C₁-C₈alkyl radical, a C₅-C₁₀cycloalkyl radical or a heteroaryl radical having 5 or 6 ring atoms, it also being possible for X and Y or R₅₀ together with one of the radicals X and Y to be the radical for completing a 5- to 7-membered ring which may contain up to 3 hetero atoms, it being possible for the ring atoms to be substituted by exocyclically double-bonded oxygen and/or by C₁-C₈alkyl and/or by C₅-C₁₀cycloalkyl radicals and/or to contain C=C double bonds;

Z is hydrogen; ammonium; an alkali metal ion; or the cation of an organic nitrogen base used for neutralisation of the free acid group.

R₅₉ and R₆₀ are each independently of the other hydrogen, C₁-C₈alkyl or C₅-C₁₀cycloalkyl; and

n and m are each independently of the other 0 or 1.

44. (new) A process for the preparation of mixtures of the organic UV filters suitable for the method defined in claim 32, wherein the UV filters, which are in micronised form, are intimately mixed together.

45. (new) A process for the preparation of mixtures of the organic UV filters suitable for the method defined in claim 32, wherein the organic UV filters are micronised in the form of mixtures of at least two single substances.

46. (new) A process for the preparation of mixtures of the organic UV filters suitable for the method defined in claim 32, wherein at least two single substances are melted together, the melt is cooled and the resulting composite is then subjected to a micronisation process.

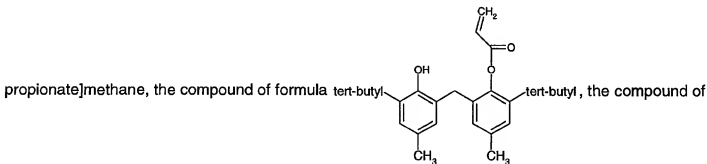
47. (new) A composite, obtained by melting together an organic UV filter as defined claim 32.

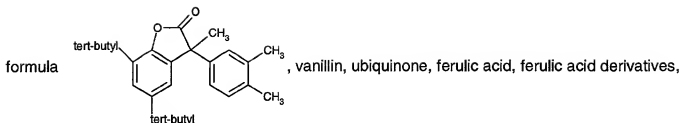
48. (new) A composite according to claim 47, wherein an inorganic pigment is additionally incorporated into the mixture.

49. (new) A composite according to claim 48, wherein the inorganic pigments are selected from TiO_2 , ZnO, iron oxides, mica and titanium or zinc salts of organic acids.

50. (new) A composite, obtained by melting together at least two of the organic UV filters defined in claim 32 and at least one antioxidant.

51. (new) A composite according to claim 50, wherein the antioxidant is selected from tocopherols, ellagic acid, propyl gallate, butylated hydroxytoluene, butylated hydroxyanisole, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)mesitylene, tetrakis[methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)-





rutinic acid, rutinic acid derivatives; urocanic acid, urocanic acid derivatives; and propolis.

52. **(new)** A composite, obtained by melting together an organic UV filter as defined in claim 32 and at least one antioxidant, and one or more inorganic pigments.

53. **(new)** A method according to claim 32, wherein a cationic or anionic compound is incorporated into the mixture.

54. **(new)** A composite, obtained by melting together an organic UV filter as defined in claim 32 and at least one cationic or anionic compound.

55. **(new)** A method according to claim 32, wherein a pharmaceutical or cosmetic active ingredient is additionally incorporated into the mixture.

56. **(new)** A cosmetic formulation, comprising an organic UV filter as defined in claim 32, optionally one or more compounds selected from the group consisting of antioxidants, inorganic pigments and cationic or anionic compounds, and also a cosmetically acceptable carrier or adjuvant.

57. **(new)** A cosmetic formulation according to claim 56, which additionally comprises an oil-soluble, non-micronised UV filter.

58. **(new)** A pharmaceutical formulation, comprising an organic UV filter as defined in claim 32, optionally one or more compounds selected from antioxidants, inorganic pigments and cationic or anionic compounds, and also a pharmaceutically acceptable carrier or adjuvant.--

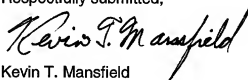
REMARKS

Since virtually all of the original claims are informal, applicants present a complete new set of claims, claims 32-58. Said claims correct the various informalities, eliminate multiple dependency and improper dependency and provide minor clarification.

Newly added claims 32-58 are supported by originally filed claims 1-31. No new matter has been added.

Applicants aver that the claims are now in proper form for examination. An Action on the merits of the claims is respectfully awaited.

Respectfully submitted,



Kevin T. Mansfield
Agent for Applicants
Reg. No. 31,635

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KTM/22037PA

DEC 14 2001

- 1 -

Micropigment mixture

The present invention relates to the use of mixtures of micronised organic UV filters in protecting human and animal skin and hair against the damaging effect of UV radiation and to their use in cosmetic and pharmaceutical formulations.

It is known that certain organic UV filters, for example sparingly soluble benzotriazole or triazine compounds, exhibit pronounced UV filtering properties when they are in the form of single compounds in micronised form. By virtue of their specific, substance-typical properties, however, they only ever absorb, reflect or scatter a certain portion of the damaging UV range.

There is strong interest in light-protective filters that cover a broad UV spectrum and thus offer better UV protection.

The aim of the present invention is therefore to find micronised organic UV filters that cover a broader portion of the UV range, with which it is thus possible to achieve better UV protection.

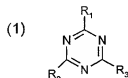
It has now been found, surprisingly, that mixtures of at least two micronised UV filters are able to achieve that aim.

The present invention therefore relates to the use of mixtures of micronised organic UV filters in protecting human and animal skin and hair against the damaging effect of UV radiation.

UV filters suitable for use according to the invention are organic, in some cases sparingly soluble, compounds, for example triazine derivatives, especially hydroxyphenyltriazine compounds or benzotriazole derivatives, amides containing a vinyl group, cinnamic acid derivatives, sulfonated benzimidazoles, Fischer base derivatives, diphenylmalonic acid dinitriles, oxalyl amides, camphor derivatives, diphenyl acrylates, para-aminobenzoic acid (PABA) and derivatives thereof, salicylates, benzophenones and further classes of sub-


stances known as UV filters.

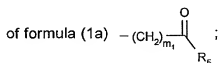
Preferred triazine derivatives suitable for use according to the invention correspond to formula



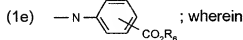
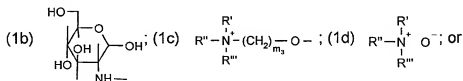
wherein

R_1 , R_2 and R_3 are each independently of the others hydrogen; OH; C_1 - C_{18} alkoxy; $-NH_2$; $-NH-R_4$; $-N(R_4)_2$; $-OR_4$,

R_4 is C_1 - C_6 alkyl; phenyl; phenoxy; anilino; pyrrolo, wherein phenyl, phenoxy, anilino and pyrrolo are unsubstituted or may be substituted by one, two or three OH groups, carboxy, $-CO-NH_2$, C_1 - C_6 alkyl or C_1 - C_6 alkoxy; a methyldene-camphor group; a group of formula $-(CH=CH)_mC(=O)-OR_4$; a group of formula  $CH=CH-C(=O)-OH$ or a corresponding alkali metal, ammonium, mono-, di- or tri- C_1 - C_4 alkylammonium, mono-, di- or tri- C_2 - C_4 alkanolammonium salt, or a C_1 - C_3 alkyl ester thereof; or a radical



R_5 is hydrogen; C_1 - C_6 alkyl unsubstituted or substituted by one or more OH groups; C_1 - C_6 alkoxy; amino; mono- or di- C_1 - C_6 alkylamino; M; a radical of formula



R' , R'' and R''' are each independently of the others C_1 - C_{14} alkyl unsubstituted or substituted by one or more OH groups;

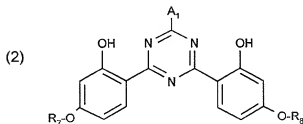
R_6 is hydrogen; M; C_1 - C_6 alkyl; or a radical of formula $-(CH_2)_{m_2}-O-T_1$;

M is a metal cation;

T_1 is hydrogen; or C_1 - C_8 alkyl;

- m is 0 or 1;
 m_2 is from 1 to 4; and
 m_3 is from 2 to 14.

Further preferred triazine derivatives suitable for use according to the invention correspond to formula



wherein

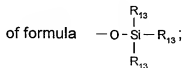
R_7 and R_8 are each independently of the other C_1 - C_{18} alkyl; C_2 - C_{18} alkenyl; a radical of formula $-CH_2-CH(OH)-CH_2-O-T_1$; or

R_7 and R_8 are a radical of formula (2a)

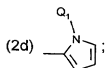
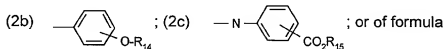
$$R_9 \left[\begin{array}{c} R_{10} \\ | \\ Si - O \\ | \\ R_{11} \end{array} \right]_{p_1} \begin{array}{c} R_{10} \\ | \\ Si - R_{12} \\ | \\ R_{11} \end{array}$$

R_9 is a direct bond; a straight-chain or branched C_1 - C_4 alkylene radical or a radical of formula $-C_{m_1}H_{2m_1+1}O-$;

R_{10} , R_{11} and R_{12} are each independently of the others C_1 - C_{18} alkyl; C_1 - C_{18} alkoxy or a radical



- R_{13} is C_1 - C_5 alkyl;
 m_1 is from 1 to 4;
 p_1 is from 0 to 5;
 A_1 is a radical of formula



R₁₄ is hydrogen; C₁-C₁₀alkyl, $-(CH_2CHR_{16}-O)_{n_1}-R_{15}$; or a radical of formula



R₁₅ is hydrogen; M; C₁-C₈alkyl; or a radical of formula $-(CH_2)_{m_2}-O-(CH_2)_{m_3}-T_1$;

R₁₆ is hydrogen; or methyl;

T₁ is hydrogen; or C₁-C₈alkyl;

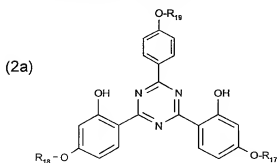
Q₁ is C₁-C₁₈alkyl;

M is a metal cation;

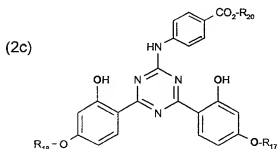
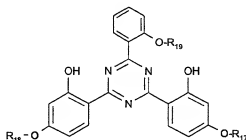
m₂ and m₃ are each independently of the other from 1 to 4; and

n₁ is from 1 to 16.

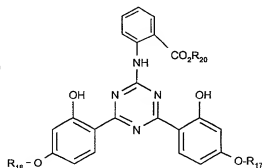
Very especially preferred triazine derivatives of formula (2) correspond to formulae



; (2b)



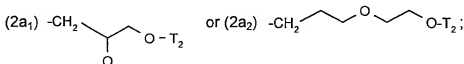
; and (2d)



wherein

R₁₇ and R₁₈ are each independently of the other C₃-C₁₈alkyl; or $-CH_2-CH(OH)-CH_2-O-T_1$;

R₁₉ is C₁-C₁₀alkyl or a radical of formula



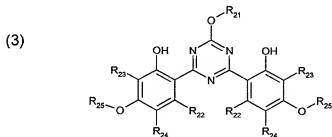
R₂₀ is hydrogen; M; C₁-C₈alkyl; $-NH-C_1-C_8$ alkyl; preferably $-NH$ -tert-alkyl; or a radical of formula $-(CH_2)_m-O-T_2$;

T₁ and T₂ are each independently of the other hydrogen; or C₁-C₅alkyl; and m is from 1 to 4.

Of very special interest are compounds of formulae (2a) and (2b) wherein R₁₇ and R₁₈ are each independently of the other C₁-C₁₈alkyl; or -CH₂-CH(-OH)-CH₂-O-T₁; R₁₉ is C₁-C₁₀alkyl; and compounds of formulae (2c) and (2d) wherein R₁₇ and R₁₈ are each independently of the other C₁-C₁₈alkyl or -CH₂-CH(-OH)-CH₂-O-T₁; and T₁ is hydrogen; or C₁-C₅alkyl.

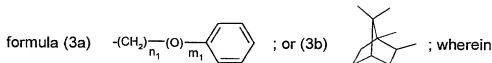
Of very great interest are triazine compounds of formulae (2a) - (2d) wherein R₁₇ and R₁₈ have the same meaning.

Further interesting triazine compounds suitable for use according to the invention correspond to formula



wherein

R₂₁ is C₁-C₃₀alkyl; C₂-C₃₀alkenyl; C₅-C₁₂cycloalkyl unsubstituted or mono- or poly-substituted by C₁-C₅alkyl; C₁-C₅alkoxy-C₁-C₁₂alkyl; amino-C₁-C₁₂alkyl; C₁-C₅-monoalkylamino-C₁-C₁₂alkyl; C₁-C₅dialkylamino-C₁-C₁₂alkyl; a radical of



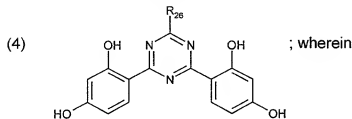
R₂₂, R₂₃ and R₂₄ are each independently of the others hydrogen, -OH; C₁-C₃₀alkyl, C₂-C₃₀alkenyl,

R₂₅ is hydrogen; or C₁-C₅alkyl;

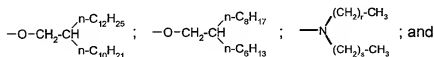
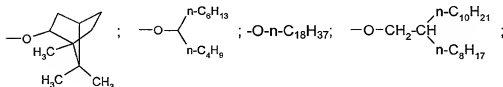
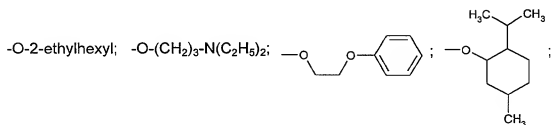
m₁ is 0 or 1; and

n_1 is from 1 to 5.

Preferred compounds correspond to formula

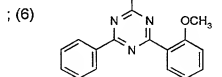
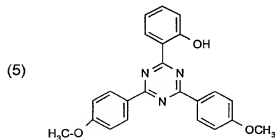


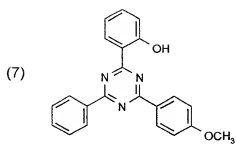
R_{26} is $-O-CH_2-CH \begin{matrix} n-C_{10}H_{21} \\ n-C_{12}H_{25} \end{matrix}$; $-O-isoc_{18}H_{38}$; $-O-CH_2-CH \begin{matrix} n-C_8H_{13} \\ n-C_8H_{17} \end{matrix}$ $-O-n-C_{18}H_{37}$; or



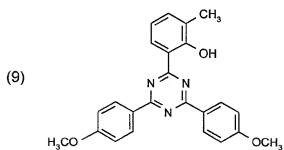
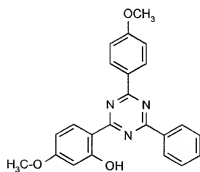
r and s are each independently of the other from 0 to 20.

Examples of triazine derivatives suitable for use according to the invention correspond to the formulae

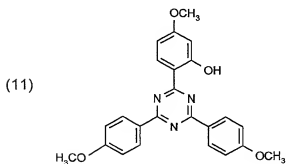
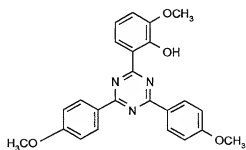




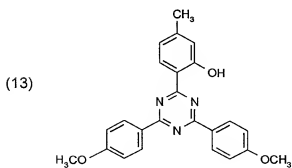
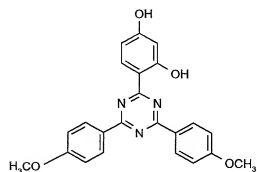
; (8)



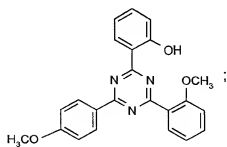
; (10)

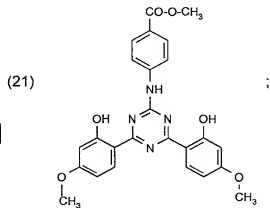
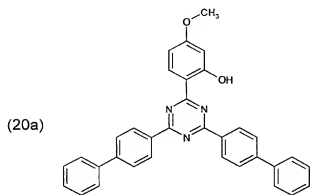
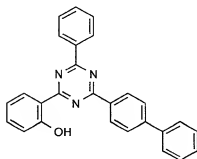
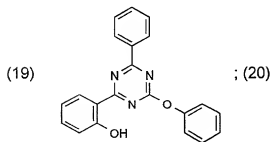
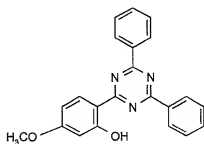
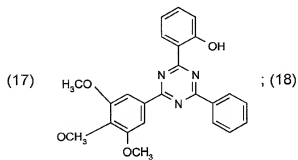
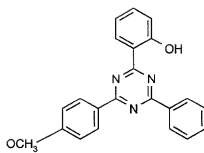
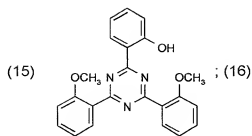


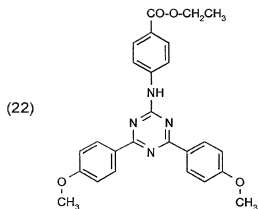
; (12)



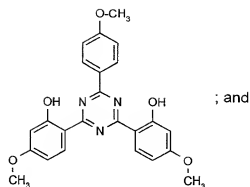
; (14)



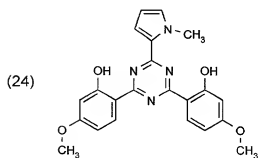




; (23)

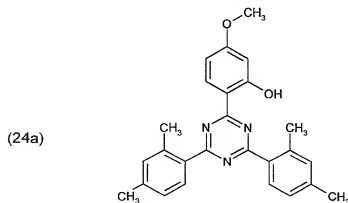


; and

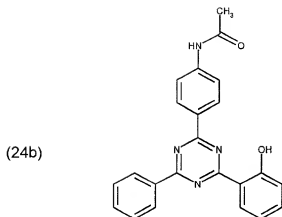


also 2,4,6-tris(diisobutyl-4'-aminobenzalmalonate)-s-triazine and 2,4-bis(diisobutyl-4-aminobenzalmalonate)-6-(4'-aminobenzylidenecamphor)-s-triazine.

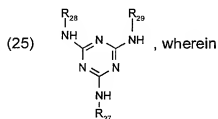
Triazine compounds suitable for use according to the invention that are likewise preferred are described in EP-A-654 469, e.g. the compound of formula



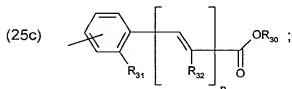
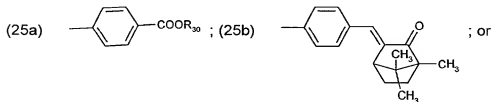
Triazine compounds especially suitable for use according to the invention are described, for example, in EP-A-0 818 450, e.g. the compound of formula



Very especially preferred triazine derivatives suitable for use according to the invention correspond to formula



R_{27} , R_{28} and R_{29} are each independently of the others a radical of formula



R_{30} is hydrogen; an alkali metal; an ammonium group $-N(R_{33})_4$,

R_{33} is hydrogen, C_1 - C_5 alkyl; or a polyoxyethylene radical that has from 1 to 10 ethylene oxide units and the terminal OH group can be etherified with a C_1 - C_5 alcohol;

R_{31} is hydrogen; -OH; or C_1 - C_6 alkoxy;

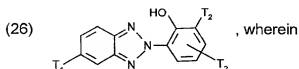
R_{32} is hydrogen or $-COOR_{30}$; and

n is 0 or 1.

When R_{30} is an alkali metal, it is especially potassium or more especially sodium. $(R_{33})_4$ is especially a mono-, di- or tri- C_1 - C_4 alkylammonium salt, a mono-, di- or tri- C_2 - C_4 alkanol-ammonium salt or a C_1 - C_3 alkyl ester thereof.

When R_{33} is a C_1 - C_3 alkyl group, it is especially a C_1 - C_2 alkyl group, more especially a methyl group, and when R_{33} is a polyoxyethylene radical, that radical contains especially from 2 to 6 ethylene oxide units.

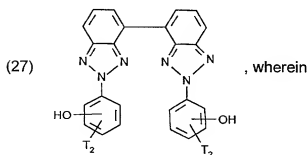
Preferred benzotriazole compounds suitable for use according to the invention correspond to formula



T_1 is C_1 - C_5 alkyl or preferably hydrogen; and

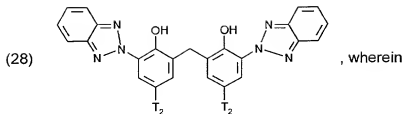
T_2 is C_1 - C_5 alkyl, preferably tert-butyl, or phenyl-substituted C_1 - C_4 alkyl, especially α, α -dimethylbenzyl.

A further preferred class of benzotriazole compounds suitable for use according to the invention corresponds to formula



T_2 is as defined for formula (26).

Further, especially preferred benzotriazole compounds suitable for use according to the invention correspond to formula



T_2 is as defined for formula (26) and is preferably methyl, tert-butyl or iso-octyl.

Preferred vinyl-group-containing amides suitable for use according to the invention correspond to formula

(29) $R_{33}-(Y)_m-CO-C(R_{34})=C(R_{35})-N(R_{36})(R_{37})$, wherein

R_{33} is C_1-C_5 alkyl, preferably methyl or ethyl, or phenyl unsubstituted or substituted by one, two or three of the radicals OH, C_1-C_5 alkyl, C_1-C_5 alkoxy and $CO-OR_{33}$;

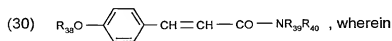
R_{34} , R_{35} , R_{36} and R_{37} are each independently of the others C_1-C_5 alkyl, preferably methyl or ethyl; or hydrogen;

Y is $-NH$ or $-O-$; and

m is as defined above.

Preferred compounds of formula (29) are 4-methyl-3-penten-2-one, ethyl 3-methylamino-2-butenate, 3-methylamino-1-phenyl-2-buten-1-one and 3-methylamino-1-phenyl-2-buten-1-one.

Preferred cinnamic acid amides suitable for use according to the invention correspond to formula



R_{38} is hydrogen or C_1-C_5 alkoxy, preferably methoxy or ethoxy;

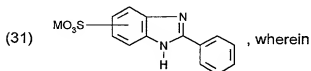
R_{39} is hydrogen or C_1-C_5 alkyl, preferably methyl or ethyl; and

R_{40} is $-(CONH)_m$ -phenyl, wherein m is as defined above and the phenyl group is unsubstituted or substituted by one, two or three of the radicals OH, C_1-C_3 alkyl, C_1-C_3 alkoxy and $CO-OR_{30}$.

R₄₀ is preferably phenyl, 4-methoxyphenyl or the phenylaminocarbonyl group.

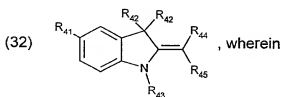
Further preferred cinnamic acid derivatives are 2-ethylhexyl-4-methoxy-cinnamate or -isoamylate or *inter alia* the cinnamic acid derivatives disclosed in US-A-5 601 811 and WO 97/00851.

Preferred sulfonated benzimidazoles suitable for use according to the invention correspond to formula



M is hydrogen or an alkali metal, preferably sodium, an alkaline earth metal, e.g. magnesium or calcium, or zinc.

Preferred Fischer base aldehydes suitable for use according to the invention correspond to formula



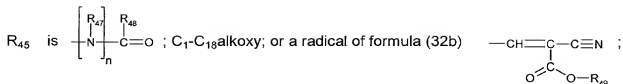
R₄₁ is hydrogen; C₁-C₅alkyl; C₁-C₁₈alkoxy; or halogen;

R₄₂ is C₁-C₈alkyl; C₅-C₇cycloalkyl; or C₆-C₁₀aryl;

R₄₃ is C₁-C₁₈alkyl or a radical of formula (32a)



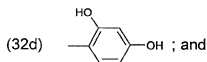
R₄₄ is hydrogen; or a radical of formula  ;



R_{46} and R_{47} are each independently of the other hydrogen; or C_1 - C_5 alkyl;

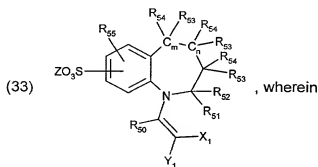
R_{48} is hydrogen; C_1 - C_5 alkyl; C_5 - C_7 cycloalkyl; phenyl; phenyl- C_1 - C_3 alkyl;

R_{49} is C_1 - C_{18} alkyl;



n is 0; or 1.

Further compounds that can preferably be used correspond to formula



R_{50} , R_{51} , R_{52} , R_{53} , R_{54} are each independently of the others hydrogen, C_1 - C_8 alkyl or C_5 - C_{10} -cycloalkyl;

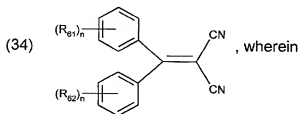
R_{55} is hydrogen; C_1 - C_8 alkyl; C_5 - C_{10} cycloalkyl; hydroxy; C_1 - C_8 alkoxy; COOR_{56} ; or $\text{CONR}_{57}\text{R}_{58}$;

R_{56} , R_{57} and R_{58} are each independently of the others hydrogen or C_1 - C_8 alkyl;

X and Y are each independently of the other hydrogen, $-\text{CN}$; CO_2R_{59} ; $\text{CONR}_{59}\text{R}_{60}$; or COR_{59} ; it being possible for the radicals X and Y additionally to be a C_1 - C_8 alkyl radical, a C_5 - C_{10} alkyl radical, especially phenyl, or a heteroaryl radical having 5 or 6 ring atoms, it also being possible for X and Y or

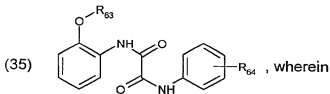
- R_{50} together with one of the radicals X and Y to be the radical for completing a 5- to 7-membered ring which may contain up to 3 hetero atoms, especially oxygen and/or nitrogen, it being possible for the ring atoms to be substituted especially by exocyclically double-bonded oxygen (keto oxygen) and/or by C_1 - C_8 alkyl and/or by C_5 - C_{10} -cycloalkyl radicals and/or to contain C=C double bonds;
- Z is hydrogen; ammonium; an alkali metal ion; especially lithium, sodium, potassium, 1/2 equivalent of an alkaline earth metal ion, preferably calcium, magnesium, or the cation of an organic nitrogen base used for neutralisation of the free acid group,
- R_{59} and R_{60} are each independently of the other hydrogen, C_1 - C_8 alkyl or C_5 - C_{10} cycloalkyl; and
- n and m are each independently of the other 0 or 1.

Preferred diphenylmalonic acid nitriles suitable for use according to the invention correspond to formula



R_{61} and R_{62} are each independently of the other C_1 - C_{12} alkyl; or C_1 - C_{12} alkoxy; and n is 0-3.

Further organic UV filters suitable for use according to the invention correspond to formula



R_{63} and R_{64} are each independently of the other C_1 - C_5 alkyl, especially ethyl.

Further preferred chemical compound classes of UV filters suitable for use according to the invention are:

- p-aminobenzoic acid derivatives (PABA), especially 2-ethylhexyl-4-dimethylamino-

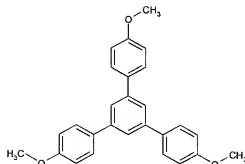
benzoate;

- salicylic acid derivatives, especially 2-ethylhexyl salicylates; homosalates; and isopropyl salicylates;
- benzophenone derivatives, especially benzophenone-2, -3 and -4;
- dibenzoylmethane derivatives, especially 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione or butylmethoxydibenzoylmethane;
- diphenyl acrylates, especially 2-ethylhexyl-2-cyano-3,3-diphenyl acrylate, ethyl 2-cyano-3,3'-diphenyl acrylate and 3-(benzofuranyl)-2-cyanoacrylate;
- 3-imidazol-4-yl-acrylic acid and 3-imidazol-4-yl acrylate;
- benzofuran derivatives, especially the p-aminophenylbenzofuran derivatives disclosed in EP-A-582 189, US-A-5 338 539 and US-A-5 518 713;
- camphor derivatives, especially 3-(4'-methyl)benzylidenebornan-2-one, 3-benzylidenebornan-2-one, N-[2(and 4)-2-oxyborn-3-ylidenemethyl]benzyl]acrylamide polymer, 3-(4'-trimethylammonium)benzylidenebornan-2-one methyl sulfate, 3,3'-(1,4-phenylene-dimethine)-bis(7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-methanesulfonic acid) and salts thereof, 3-(4'-sulfo)benzylidenebornan-2-one and salts thereof, and also
- menthyl o-aminobenzoate.

Preferably the following mixtures of organic UV filters are used:

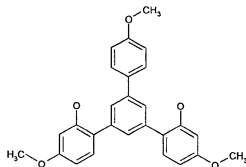
- mixtures of methylene bis-benzotriazolyl tetramethylbutylphenol and octyl triazone;
- mixtures of octyl triazone and methylene bis-benzotriazolyl tetramethylbutylphenol;
- mixtures of 2-[(2,4-methoxy)-phenyl]-4,6-bis[(2-hydroxy-4-methoxy)-phenyl]-(1,3,5)-triazine and methylene bis-benzotriazolyl tetramethylbutylphenol;
- mixtures of methylene bis-benzotriazolyl tetramethylbutylphenol and dioctyl butamido-triazone;
- mixtures of methylene bis-benzotriazolyl tetramethylbutylphenol and octyl-2,2'-methylene bis[6-(2H-benzotriazol-2-yl)-4-methyl-phenol],
- mixtures of octyl triazone and tris-resorcinyll triazine;
- mixtures of 2,2'-methylene bis[6-(2H-benzotriazol-2-yl)-4-methyl-phenol], octyl triazone

and the compound of formula (36)



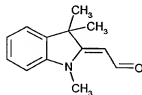
- mixtures of 2,2'-methylene bis[6-(2H-benzotriazol-2-yl)-4-methyl-phenol, octyl triazone

and the compound of formula (37)



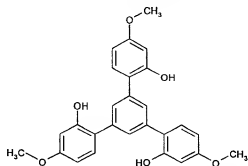
- mixtures of methylene bis-benzotriazolyl tetramethylbutylphenol, octyl triazone and the

compound of formula (38)



- mixtures of methylene bis-benzotriazolyl tetramethylbutylphenol and the compound of

formula (39)



- mixtures of methylene bis-benzotriazolyl tetramethylbutylphenol, dioctyl butamido-triazone and the compound of formula (37).

In the radicals defined above, C₁-C₁₈alkyl denotes straight-chain or branched alkyl radicals, e.g. methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, amyl, isoamyl or tert-

amyl, heptyl, octyl, isoctyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl.

C₁-C₁₈Alkoxy radicals are straight-chain or branched alkyl radicals, e.g. methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, tert-butoxy, amyloxy, isoamyloxy or tert-amyloxy, heptyloxy, octyloxy, isoctyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, tetradecyloxy, pentadecyloxy, hexadecyloxy, heptadecyloxy and octadecyloxy.

C₂-C₁₈Alkenyl is e.g. allyl, methallyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl, n-oct-2-enyl, n-dodec-2-enyl, isododecenyl, n-dodec-2-enyl or n-octadec-4-enyl.

The mixtures of micronised organic UV filters suitable for use according to the invention can be prepared in various ways:

In a first method, at least two of the above-mentioned organic UV filters can be mixed, as single substances, during the process for the preparation of the microparticles (micronisation).

A further possible preparation method comprises intimately mixing together the single substances of the UV filters which have already been micronised.

A third possible preparation method comprises melting together at least two of the UV filters mentioned above. After the melt has cooled, a homogeneous composite is obtained, which is micronised in customary manner.

The invention relates also to the homogeneous composites of at least two organic UV filters.

The invention relates also to composites obtainable by melting one or more inorganic micropigments into one or more organic UV filters.

Examples of micropigments are TiO₂, ZnO, iron oxides and other inorganic oxides, mica and other suitable inorganic minerals, and also titanium salts, alkaline earth metal salts and zinc

salts of organic acids.

As a result, the undesirable photocatalytic properties of some of those inorganic micro-pigments (TiO_2 , ZnO) can be suppressed at the same time and their positive properties additionally fully utilised.

Advantageously the above-mentioned inorganic UV filters are melted into methylene bis-benzotriazolyl tetramethylbutylphenol. The composite so obtained is then micronised in customary manner.

The invention relates also to composites obtainable by melting at least two electrically neutral organic UV filters with cationically or anionically charged compounds.

For that purpose, cationically or anionically charged compounds are melted with the corresponding organic, electrically neutral UV filters and then cooled. By means of that process it is possible in the subsequent micronisation step to prepare organic UV filter pigments that are permanently provided with a positive or negative charge. Such provision effectively prevents the aggregation of the micronised particles in the sunscreen preparations, which may occur when the particle diameter is $< 1 \mu\text{m}$. Providing the particles with a "coating" having a repellent effect, which is otherwise customary, is then superfluous in some cases.

As cationically or anionically charged compounds it is possible to use UV filters or other compounds having one or more cationic or anionic groupings, e.g.

- N,N,N-trimethyl-4-(2-oxoborn-3-ylidenemethyl)-aniline methyl sulfate;
- camphor benzalkonium methosulfate;
- fatty amines;
- betaines, e.g. cocamidopropyl betaine;
- quats, e.g. ricinoleamidopropyltrimodium methosulfate, Quaternium 18 or cetyltrimethylammonium bromide;
- behenic acid and other organic acids, e.g. isostearic acid, citric acid monoglyceride or sodium methylcocoyl taurate;
- phospholipids, e.g. phosphatidylcholine, phosphatidylserine or alkylamine oxide;

- ceramides and pseudoceramides and phytosterols.

The last-mentioned compounds impart oleophobic properties to the micronised UV filters.

The proportion of cationic or anionic compounds in the composite is from 0.001 to 5 % by weight, preferably from 0.01 to 3 % by weight, based on the weight of the UV filter(s).

The invention relates also to composites obtainable by melting at least one sparingly soluble or insoluble organic UV filter with antioxidants.

For that purpose, the sparingly soluble or insoluble organic UV filter(s) is/are melted together with antioxidants, cooled and then micronised in customary manner.

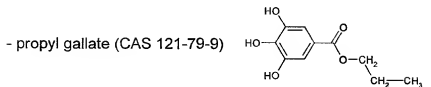
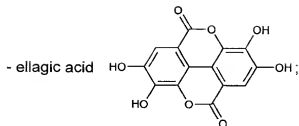
Antioxidants suitable for use according to the invention include all organic substances having scavenger properties that can be melted together with organic UV filters. New micropigments are obtained that offer simultaneously UV protection and an antioxidative action on their surface. That property is desirable in the case of cosmetic sunscreens, because the influence of UV and light can bring about the formation of damaging free radicals both in formulations and on the skin, which can result, for example, in so-called Mallorca acne or in premature skin ageing. Providing the micronised UV filters with antioxidants, in addition to giving protection against UV damage, simultaneously provides protection against photochemical degradation of constituents of the sunscreen formulation.

The proportion of antioxidants in the composite is generally from 0.001 to 30 % by weight, preferably from 0.01 to 3 % by weight, based on the weight of the UV filter(s).

A content of antioxidants in micropigments is especially advantageous when the latter comprise, in addition to organic UV filters, also the above-mentioned photocatalytically active inorganic micropigments, e.g. titanium dioxide, zinc oxide (also coated) or other suitable inorganic oxides, e.g. iron oxide.

The following compounds may be mentioned as examples of antioxidants:

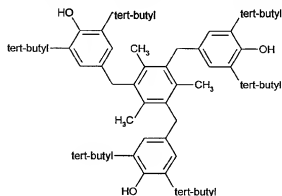
- tocopherols, e.g. α -tocopherol (CAS 59-02-9), tocopheryl acetate, vitamin E succinate,



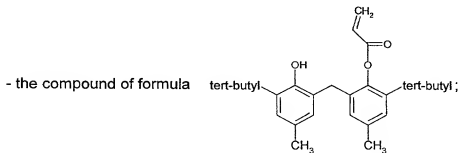
- N-butylated hydroxytoluene (BHT; CAS 128-37-0);

- butylated hydroxyanisole (BHA);

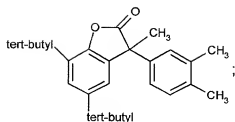
- 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)mesitylene (CAS 1709-70-2)



- tetrakis[methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane (CAS 6683-19-8);



- the compound of formula

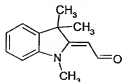


- vanillin;
- ubiquinone;
- ferulic acid and derivatives;
- rutinic acid and derivatives;
- urocanic acid and derivatives; and
- propolis.

Preferably the following mixtures of antioxidants and organic UV filters are used:

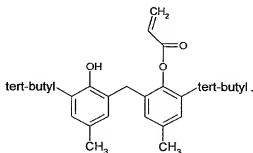
- mixtures of methylene bis-benzotriazolyl tetramethylbutylphenol, octyl triazone, titanium dioxide and tocopherol,
- mixtures of 2,2'-methylene bis[6-(2H-benzotriazol-2-yl)-4-methyl-phenol, octyl triazone, tris-resorcinyol triazine and vitamin E
- mixtures of methylene bis-benzotriazolyl tetramethylbutylphenol, octyl triazone, the

compound of formula (103)



("Fischer aldehyde") and the

compound of formula



The invention relates also to composites obtainable by melting meltable cosmetic, plant-based and pharmaceutical active ingredients into organic UV filters.

In general it is possible to use micronised UV filters as carriers of highly active substances,

especially cosmetic and/or pharmaceutical active ingredients. The advantage of such composites lies in the possibility of releasing the active ingredient(s) from the solids (slow release). Slow release ensures that highly active substances, e.g. anti-inflammatories, cosmetic active ingredients or trace elements, e.g. Zn^{2+} or Mg^{2+} , are also uniformly effective over the entire period of use of the UV pigments.

Examples of active ingredients that may be used include:

- active ingredients for providing antimicrobial properties and, simultaneously, anti-inflammatory action, e.g. triclosan or diclosan;
- anti-inflammatory active ingredients, e.g. farnesol, panthenol and avocado oil;
- active ingredients having a deodorant or antiperspirant action, e.g. zinc ricinoleates and alkyl citrates,
- undecylenic acid and derivatives thereof (e.g. diethanolamides)
- zinc undecylate;
- pyrithiones, e.g. sodium pyrithione;
- odorants or odorant mixtures incorporated by melting, e.g. menthol, geraniol etc., that impart a permanent odour of uniform intensity to such micropigments and to formulations comprising them.

For the preparation of the micropigment mixtures it is possible to use any known processes that are suitable for the preparation of microparticles, e.g.:

- wet-grinding with a hard grinding medium, for example zirconium silicate and a protective surfactant or a protective polymer in water or in a suitable organic solvent;
- spray-drying from a suitable solvent, for example aqueous suspensions or suspensions containing organic solvents, or true solutions in water, ethanol, dichloroethane, toluene or N-methylpyrrolidone etc..
- by the expansion according to the RESS process (Rapid Expansion of Supercritical Solutions) of supercritical fluids (e.g. CO_2) in which the UV filter(s) is/are dissolved, or the expansion of fluid carbon dioxide together with a solution of one or more UV filters in a suitable organic solvent;
- by reprecipitation from suitable solvents, including supercritical fluids (GASR process = Gas Anti-Solvent Recrystallisation / PCA process = Precipitation with Compressed Anti-solvents).

As grinding apparatus for the preparation of the micronised organic UV absorbers according to the invention there may be used, for example, a jet mill, ball mill, vibratory mill or hammer mill, preferably a high-speed mixing mill. The grinding is preferably carried out with a grinding aid, for example an alkylated vinylpyrrolidone polymer, a vinylpyrrolidone/vinyl acetate copolymer, an acyl glutamate, an alkyl polyglucoside, cetareth-25 or especially a phospholipid.

The micropigments and mixtures of micropigments so obtained generally have an average particle size of from 0.02 to 2 nm, preferably from 0.05 to 1.5 nm and more especially from 0.1 to 1.0 nm.

By virtue of their lipophilicity, they can satisfactorily be incorporated, alone or together with other soluble organic UV absorbers, into oil-containing and fat-containing cosmetic formulations, such as oils, O/W or W/O emulsions, fatty sticks or gels, in accordance with known methods.

Surprisingly, the formulations obtained have the same or better protective action when soluble UV absorbers are used in smaller amounts or even not at all.

The invention relates also to a cosmetic formulation comprising a mixture of micropigments, optionally one or more antioxidants and/or inorganic pigments and/or a cationic or anionic compound, and also cosmetically acceptable carriers or adjuvants.

Cosmetic formulations according to the invention may be contained in a wide variety of cosmetic preparations. Especially the following preparations, for example, come into consideration:

- skin-care preparations, e.g. skin-washing and cleansing preparations in the form of tablet-form or liquid soaps, synthetic detergents or washing pastes;
- bath preparations, e.g. liquid (foam baths, milks, shower preparations) or solid bath preparations, e.g. bath cubes and bath salts;
- skin-care preparations, e.g. skin emulsions, multi-emulsions or skin oils;
- cosmetic personal care preparations, e.g. facial make-up in the form of day creams or

powder creams, face powder (loose or pressed), rouge or cream make-up, eye-care preparations, e.g. eyeshadow preparations, mascara, eyeliner, eye creams or eye-fix creams; lip-care preparations, e.g. lipsticks, lip gloss, lip contour pencils, nail-care preparations, such as nail varnish, nail varnish removers, nail hardeners or cuticle removers;

- intimate hygiene preparations, e.g. intimate washing lotions or intimate sprays;
- foot-care preparations, e.g. foot baths, foot powders, foot creams or foot balsams, special deodorants and antiperspirants or callus-removing preparations;
- light-protective preparations, such as sun milks, lotions, creams and oils, sun blocks or tropicals, pre-tanning preparations or after-sun preparations;
- skin-tanning preparations, e.g. self-tanning creams;
- depigmenting preparations, e.g. preparations for bleaching the skin or skin-lightening preparations;
- insect-repellents, e.g. insect-repellent oils, lotions, sprays or sticks;
- deodorants, such as deodorant sprays, pump-action sprays, deodorant gels, sticks or roll-ons;
- antiperspirants, e.g. antiperspirant sticks, creams or roll-ons;
- preparations for cleansing and caring for blemished skin, e.g. synthetic detergents (solid or liquid), peeling or scrub preparations or peeling masks;
- hair-removal preparations in chemical form (depilation), e.g. hair-removing powders, liquid hair-removing preparations, cream- or paste-form hair-removing preparations, hair-removing preparations in gel form or aerosol foams;
- shaving preparations, e.g. shaving soap, foaming shaving creams, non-foaming shaving creams, foams and gels, pre shave preparations for dry shaving, aftershaves or after-shave lotions;
- fragrance preparations, e.g. fragrances (eau de Cologne, eau de toilette, eau de parfum, parfum de toilette, perfume), perfume oils or cream perfumes;
- dental-care, denture-care and mouth-care preparations, e.g. toothpastes, gel tooth-pastes, tooth powders, mouthwash concentrates, anti-plaque mouthwashes, denture cleaners or denture fixatives;
- cosmetic hair-treatment preparations, e.g. hair-washing preparations in the form of shampoos and conditioners, hair-care preparations, e.g. pretreatment preparations, hair tonics, styling creams, styling gels, pomades, hair rinses, treatment packs, intensive hair

treatments, hair-structuring preparations, e.g. hair-waving preparations for permanent waves (hot wave, mild wave, cold wave), hair-straightening preparations, liquid hair-setting preparations, foams, hairsprays, bleaching preparations, e.g. hydrogen peroxide solutions, lightening shampoos, bleaching creams, bleaching powders, bleaching pastes or oils, temporary, semi-permanent or permanent hair colourants, preparations containing self-oxidising dyes, or natural hair colourants, such as henna or camomile.

The final formulations listed may be in a wide variety of presentation forms, for example:

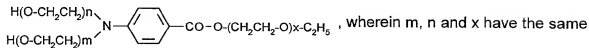
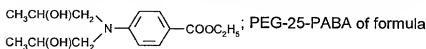
- in the form of liquid preparations as a W/O, O/W, O/W/O, W/O/W or PIT emulsion and all kinds of microemulsions,
- in the form of a gel,
- in the form of an oil, a cream, milk or lotion,
- in the form of a powder, a lacquer, a tablet or make-up,
- in the form of a stick,
- in the form of a spray (spray with propellant gas or pump-action spray) or an aerosol,
- in the form of a foam, or
- in the form of a paste.

Advantageously the cosmetic formulations according to the invention may comprise further substances that absorb UV radiation in the UVB range. In that case the total amount of filter substances is from 0.1 to 30 % by weight, preferably from 0.5 to 10 % by weight, especially from 1 to 6 % by weight, based on the total weight of the composition.

As additional UVB filters there come into consideration especially oil-soluble, non-micronised compounds, e.g. organic UV absorbers from the class of the p-aminobenzoic acid derivatives, salicylic acid derivatives, benzophenone derivatives, dibenzoylmethane derivatives, diphenyl acrylate derivatives, benzofuran derivatives, polymeric UV absorbers, comprising one or more organosilicon radicals, cinnamic acid derivatives, camphor derivatives, trianilino-s-triazine derivatives, phenylbenzimidazolesulfonic acid and salts thereof, menthyl anthranilates, benzotriazole derivatives, and/or an inorganic micropigment selected from TiO_2 , zinc oxide and mica, each encapsulated with aluminium oxide or silicon dioxide.

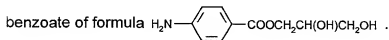
- The following compounds are examples of p-aminobenzoic acid derivatives:

4-aminobenzoic acid (PABA); ethyldihydroxypropyl-PABA of formula



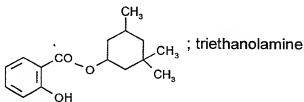
meanings and are each a maximum of 25;

octyldimethyl PABA of formula $(\text{CH}_3)_2\text{N}(\text{CH}_2)_7\text{C}_6\text{H}_4\text{COO-isooctyl}$; and glycyl amino-



- The following compounds are examples of salicylic acid derivatives:

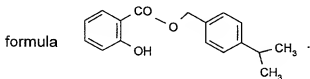
homomenthyl salicylate of formula



salicylate of formula $\text{C}_6\text{H}_4(\text{OH})\text{COO}^- + \text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$; amyl p-dimethylaminobenzoate

of formula (10) $(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4\text{COO-amyl}$; octyl salicylate of

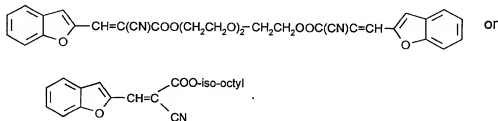
formula $\text{C}_6\text{H}_4(\text{OH})\text{COO-isooctyl}$; and 4-isopropylbenzyl salicylate of



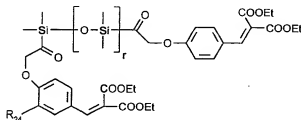
- The following compounds are examples of benzophenone derivatives:

benzophenone-3-(2-hydroxy-4-methoxybenzophenone), benzophenone-4-(2-hydroxy-4-methoxybenzophenone-5-sulfonic acid) and benzophenone-8-(2,2'-dihydroxy-4-methoxybenzophenone).

- The following compound is an example of a dibenzoylmethane derivative:
butylmethoxydibenzoylmethane-[1-(4-tert-butyl)-3-(4-methoxyphenyl)propane-1,3-dione].
- The following compounds are examples of diphenyl acrylate derivatives:
octocrylene (2-ethylhexyl-2-cyano-3,3'-diphenyl acrylate) and etocrylene (ethyl-2-cyano-3,3'-diphenyl acrylate).
- The following compounds are examples of benzofuran derivatives:
3-(benzofuranyl)-2-cyanoacrylate, 2-(2-benzofuranyl)-5-tert-butylbenzoxazole and 2-(p-aminophenyl)benzofuran and especially the compound of formula



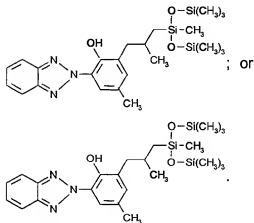
- The following compounds are examples of polymeric UV absorbers that contain one or more organosilicon radicals:
a benzylidene malonate derivative, especially the compound of formula



wherein

R_{24} is hydrogen or methoxy and

r is approximately 7; the compound of formula



- The following compounds are examples of cinnamic acid esters:
octyl methoxycinnamate (4-methoxycinnamic acid 2-ethylhexyl ester), diethanolamine methoxycinnamate (diethanolamine salt of 4-methoxycinnamic acid), isoamyl p-methoxycinnamate (4-ethoxycinnamic acid 2-isoamyl ester), 2,5-diisopropylmethyl cinnamate and a cinnamic acid amido derivative.
- The following compounds are examples of camphor derivatives:
4-methyl-benzylidene camphor [3-(4'-methyl)benzylidene-bornan-2-one], 3-benzylidene camphor (3-benzylidene-bornan-2-one), polyacrylamidomethylbenzylidene camphor {N-[2(and 4)-2-oxyborn-3-ylidene-methyl]benzyl]acrylamide polymer}, trimonium-benzylidene camphor sulfate [3-(4'-trimethylammonium)-benzylidene-bornan-2-one methyl sulfate], terephthalidene dicamphorsulfonic acid {3,3'-(1,4-phenylenedimethine)-bis(7,7-dimethyl-2-oxo-bicyclo[2.2.1]heptane-1-methanesulfonic acid) } or salts thereof, and benzylidene camphorsulfonic acid [3-(4'-sulfo)benzylidene-bornan-2-one] or salts thereof.
- The following compounds are examples of trianilino-s-triazine derivatives:
octyl triazine-[2,4,6-trianilino-(p-carbo-2'-ethyl-1'-oxy)-1,3,5-triazine, and the trianilino-s-triazine derivatives described in US-A-5 332 568, US-A-5 252 323, WO 93/17002 and WO 97/03642 and EP-A-0 517 104.
- The following compound is an example of a benzotriazole:
2-(2-hydroxy-5-methyl-phenyl)benzotriazole.

The following Examples serve to illustrate the invention but do not limit the invention thereto. The cosmetic active substances are primarily given with their INCI name (INCI = International Norm of Cosmetics Ingredients).

Example 1:

50 parts of methylene bis-benzotriazolyl tetramethylbutylphenol and 50 parts of octyl triazone are ground together with a grinding medium of zirconium silicate sand, a protective surfactant (alkyl polyglucoside) and water in a bead mill to form a mixed micropigment having a d_{50} of 190 nm. When the grinding medium has been separated off, the suspension of the mixed micropigment can be used in the preparation of sunscreen formulations.

Example 2:

32 parts of octyl triazone, 1 part of cetyltrimethylammonium bromide and 66 parts of methylene bis-benzotriazolyl tetramethylbutylphenol are melted together homogeneously. The melt is rapidly cooled to room temperature and the solidified melt is comminuted mechanically (hammer mill). The powder so obtained is suspended in water; decyl glycoside is added and the mixture is micronised together with a grinding aid ('heavy sand') to a particle size of d_{50} 200 nm diameter. When the grinding aid has been separated off, an aqueous suspension of the micronised UV absorber composite is obtained. The suspension is rendered slightly acidic with citric acid and can be used in the preparation of cosmetic and pharmaceutical formulations.

Example 3:

25 parts of 2-[(2,4-methoxy)-phenyl]-4,6-bis[(2-hydroxy-4-methoxy)-phenyl]-(1,3,5)-triazine, 74 parts of methylene bis-benzotriazolyl tetramethylbutylphenol and 1 part of tetrakis-[methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane are melted together homogeneously. The melt is rapidly cooled to room temperature and the solidified melt is comminuted mechanically (hammer mill). The powder so obtained is suspended in water; first decyl glycoside and then, after further grinding, cetareth-25 are added and the mixture is micronised together with a grinding aid ('heavy sand') to a particle size of d_{50} 190 nm diameter. When the grinding aid has been separated off, an aqueous suspension of the micronised UV absorber composite is obtained which can be used in the preparation of

cosmetic and pharmaceutical formulations.

Example 4:

25 parts of dioctyl butamidotriazone are dissolved in 75 parts of molten methylene bis-benzotriazolyl tetramethylbutylphenol. The mixture is cooled rapidly, comminuted mechanically to form a fine powder and then ground with a grinding medium of zirconium silicate sand, a protective surfactant (phospholipid) and water to form a micropigment of d_{50} 300 nm. The suspension of the micropigment is separated from the grinding medium and used in the preparation of sunscreen formulations.

Example 5:

24 parts of octyl triazone, 5 parts of titanium dioxide and one part of tocopherol are mixed into 70 parts of molten methylene bis-benzotriazolyl tetramethylbutylphenol. The mixture is cooled rapidly, comminuted mechanically to form a fine powder and then ground with a grinding medium of zirconium silicate sand, a protective surfactant (alkyl polyglucoside) and water to form a micropigment. The suspension of the micropigment is separated from the grinding medium and used in the preparation of sunscreen formulations.

In the following Examples 6 to 11, suspensions of microcomposites of the following compositions are prepared analogously to Examples 1 and 2:

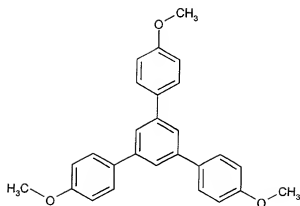
Example 6:

60 parts of 2,2'-methylene bis[6-(2H-benzotriazol-2-yl)-4-methyl-phenol],
20 parts of octyl triazone, 19 parts of tris-resorciny l triazine and 1 part of vitamin E, adjusted to pH 6.5 with citric acid.

Example 7:

60 parts of 2,2'-methylene bis[6-(2H-benzotriazol-2-yl)-4-methyl-phenol],
20 parts of octyl triazone and 20 parts of the compound of formula

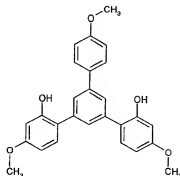
(101)



Example 8:

59 parts of 2,2'-methylene bis[6-(2H-benzotriazol-2-yl)-4-methyl-phenol],
20 parts of octyl triazone,

20 parts of the compound of formula (102)

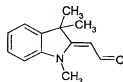


adjusted to pH 6.5 with citric acid.

Example 9:

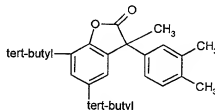
75 parts of methylene bis-benzotriazolyl tetramethylbutylphenol,
10 parts of octyl triazone (grinding at pH < 5, adjusted with citric acid),

14 parts of the compound of formula (103)



("Fischer aldehyde") and

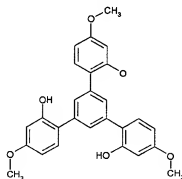
1 part of the compound of formula



Example 10:

80 parts of methylene bis-benzotriazolyl tetramethylbutylphenol, and

20 parts of the compound of formula (104)



Example 11:

50 parts of methylene bis-benzotriazolyl tetramethylbutylphenol,

10 parts of dioctyl butamidotriazone (grinding at pH < 5, adjusted to pH 6.5 with citric acid)
and

20 parts of the compound of formula (102).

Example 12: O/W Sunscreen lotion

		%
A	Polyglyceryl-3 methylglucose distearate	2.0
	Decyl oleate	5.7
	Isopropyl palmitate	6.0
	Caprylic/capric triglyceride	7.5
B	Glycerol	3.0
	Phenonip	0.5
	Water	69.3
C	Carbomer	0.2
	Isopropyl palmitate	0.8
D	Micropigment from Example 2	5.0
E	NaOH (10%)	as required

Example 13: O/W Emulsion

	%
Potassium cetyl phosphate	2.00
Tricontanyl PVP	1.00
Caprylic/capric triglyceride	5.00
Cetearyl isononanoate	5.00
C ₁₂₋₁₅ Alkyl benzoate	5.00
Glyceryl stearate	3.00
Cetyl alcohol	1.00
Phenoxyethanol & parabens	1.00
Octyl methoxycinnamate	5.00
Dimethicone	0.10
Deionised water	64.15
Carbomer (Carbopol 981)	0.10
Glycerol	3.00
NaOH (10%)	1.00
Micropigment from Example 1	4.00

Example 14: O/W Emulsion:

	%
Cetearyl alcohol & dicetyl phosphate & ceteth-10 phosphate	6.00
Caprylic/capric triglyceride	5.00
Cetearyl isononanoate	5.00
C ₁₂₋₁₅ Alkyl benzoate	5.00
Phenoxyethanol & parabens	1.00
Octyl methoxycinnamate	5.00
Dimethicone	0.20
Deionised water	64.70
Carbomer (Carbopol 981)	0.10
Glycerol	3.00
NaOH (10%)	0.65
Micropigment from Example 3	4.00

Example 15: O/W Emulsion:

	%
Isopropyl myristate & triaureth-4 phosphate	5.00
Tricantanyl PVP	1.00
Caprylic/capric triglyceride	5.00
Cetearyl isononanoate	2.00
C ₁₂₋₁₅ Alkyl benzoate	5.00
Glyceryl stearate	2.00
Cetyl alcohol	1.00
Phenoxyethanol & parabens	1.00
Octyl methoxycinnamate	5.00
Dimethicone	0.10
Deionised water	66.30
Carbomer (Carbopol 981)	0.10
Glycerol	3.00
NaOH (10%)	0.50
Micropigment from Example 4	4.00

Example 16: O/W Emulsion

	%
Sodium stearyl lactate tricantanyl PVP	1.50
Tricantanyl PVP	1.00
Caprylic/capric triglyceride	5.00
Cetearyl isononanoate	5.00
C ₁₂₋₁₅ Alkyl benzoate	5.00
Glyceryl stearate	3.50
Cetyl alcohol	2.00
Phenoxyethanol & parabens	1.00
Octyl methoxycinnamate	5.00
Dimethicone	0.20
Deionised water	63.60
Carbomer (Carbopol 981)	0.10
Glycerol	3.00
NaOH (10%)	0.10
Micropigment from Example 6	4.00

Example 17: O/W Emulsion

	%
Cetearyl alcohol & sodium cetearyl sulfate	5.00
Caprylic/capric triglyceride	5.00
Cetearyl isononanoate	5.00
C ₁₂₋₁₅ Alkyl benzoate	5.00
Phenoxyethanol & parabens	1.00
Octyl methoxycinnamate	5.00
Dimethicone	0.10
Deionised water	65.90
Glycerol	3.00
NaOH (10%)	0.30
Micropigment from Example 9	4.00

Example 18: O/W Emulsion

	%
Lauryl glucoside & polyglyceryl-2 dihydroxystearate & glycerol	3.00
Tricontanyl PVP	1.00
Caprylic/capric triglyceride	4.00
Cetearyl isononanoate	4.00
C ₁₂₋₁₅ Alkyl benzoate	5.00
Glyceryl stearate	2.00
Cetyl alcohol	3.00
Phenoxyethanol & parabens	1.00
Octyl methoxycinnamate	5.00
Dimethicone	0.20
Deionised water	64.49
Carbomer (Carbopol 981)	0.10
Glycerol	3.00
NaOH (10%)	0.21
Micropigment from Example 8	4.00

Example 19: O/W Emulsion:

	%
Cetaryl glucoside & cetearyl alcohol	4.50
Tricantanyl PVP	1.00
Caprylic/capric triglyceride	5.00
Cetearyl isononanoate	5.00
C ₁₂₋₁₅ Alkyl benzoate	5.00
Phenoxyethanol & parabens	1.00
Octyl triazone	3.00
4-Methylbenzylidene camphor	3.00
Dimethicone	0.20
Deionised water	64.65
Steareth-10 allyl ether(acrylates copolymer	5.00
Glycerol	3.00
NaOH (10%)	1.00
Micropigment from Example 2	4.00

Example 20: O/W Emulsion

	%
Cetaryl glucoside	5.00
Tricantanyl PVP	1.00
Caprylic/capric triglyceride	5.00
Cetearyl isononanoate	5.00
C ₁₂₋₁₅ Alkyl benzoate	5.00
Phenoxyethanol & parabens	1.00
Octocrylene	3.00
Octyl methoxycinnamate	4.00
Dimethicone	0.20
Deionised water	63.15
Carbomer (Carbopol 981)	0.50
Glycerol	3.00
NaOH (10%)	0.15
Micropigment from Example 2	4.00

Example 21: O/W Emulsion:

	%
Polyglyceryl-10 petastearate & behenyl alcohol & sodium stearoyl laurate	2.50
Caprylic/capric triglyceride	5.00
Cetearyl isononanoate	5.00
C ₁₂₋₁₅ Alkyl benzoate	5.00
Glyceryl stearate	3.00
Cetearyl alcohol	2.00
Phenoxyethanol & parabens	1.00
Octyl methoxycinnamate	5.00
Dimethicone	0.20
Deionised water	64.75
Carbomer (Carbopol 981)	0.15
Glycerol	3.00
NaOH (10%)	0.40
Micropigment from Example 9	4.00

Example 22: O/W Emulsion:

	%
Palmitic acid & stearic acid	1.80
Glyceryl stearate SE	3.00
Tricontanyl PVP	1.00
Caprylic/capric triglyceride	5.00
Cetearyl isononanoate	5.00
C ₁₂₋₁₅ Alkyl benzoate	5.00
Glyceryl stearate	0.50
Phenoxyethanol & parabens	1.00
Octyl dimethyl PABA	5.00
Dimethicone	0.10
Deionised water	64.15
Carbomer (Carbopol 981)	0.10
Glycerol	3.00
NaOH (10%)	0.50
Micropigment from Example 1	4.00

Example 23: O/W Emulsion:

	%
Glyceryl stearate & PEG 100 stearate	3.00
Tricontanyl PVP	1.00
Caprylic/capric triglyceride	5.00
Cetearyl isononanoate	5.00
C ₁₂₋₁₅ Alkyl benzoate	5.00
Cetearyl alcohol	3.00
Phenoxyethanol & parabens	1.00
Octyl methoxycinnamate	5.00
Dimethicone	0.10
Deionised water	64.60
Carbomer (Carbopol 981)	0.10
Glycerol	3.00
NaOH (10%)	0.20
Micropigment from Example 3	4.00

Example 24: O/W Emulsion:

	%
Steareth-2	2.50
Steareth-21	1.00
Tricontanyl PVP	1.00
Caprylic/capric triglyceride	5.00
Cetearyl isononanoate	5.00
C ₁₂₋₁₅ Alkyl benzoate	5.00
Cetyl alcohol	1.00
Phenoxyethanol & parabens	1.00
Methyl anthranilate	3.00
Octyl methoxycinnamate	4.00
Dimethicone	0.10
Deionised water	63.95
Carbomer (Carbopol 981)	0.20
Glycerol	3.00
NaOH (10%)	0.25
Micropigment from Example 4	4.00

Example 25: O/W Emulsion:

	%
Glyceryl stearate & cetareth-20 & cetareth-12 & cetyl alcohol & cetyl palmitate	5.00
Tricontanyl PVP	1.00
Caprylic/capric triglyceride	5.00
Cetearyl isononanoate	5.00
C ₁₂₋₁₅ Alkyl benzoate	5.00
Phenoxyethanol & parabens	1.00
4-methylbenzylidene camphor	5.00
Dimethicone	0.10
Deionised water	65.60
Carbomer (Carbopol 981)	0.10
Glycerol	3.00
NaOH (10%)	0.20
Micropigment from Example 3	4.00

Example 26: O/W Emulsion

	%
Octyldecyl phosphate	3.00
Tricontanyl PVP	1.00
Caprylic/capric triglyceride	5.00
Cetearyl isononanoate	5.00
C ₁₂₋₁₅ Alkyl benzoate	5.00
Phenoxyethanol & parabens	1.00
Octyl methoxycinnamate	5.00
Dimethicone	0.10
Deionised water	64.50
Sodium cocoyl glutamate	0.60
Feareth-10 allyl ether/ acrylates copolymer	0.50
Glycerol	3.00
NaOH (10%)	2.30
Micropigment from Example 4	4.00

Example 27: O/W Emulsion:

	%
Polyglyceryl-3 methyl glucose distearate	2.00
Tricontanyl PVP	1.00
Tocopherol & ascorbyl palmitate & ascorbic acid & citric acid & PEG-8	0.05
Decyl oleate	4.50
Isopropyl palmitate	6.00
Caprylic/capric triglyceride	5.00
Glyceryl stearate	1.00
Cetearyl alcohol	1.00
2-[(2,4-Methoxy)-phenyl]-4,6-bis[(2-hydroxy-4-methoxy)-phenyl]-(1,3,5)-triazine	2.00
Octyl methoxycinnamate	3.00
Deionised water	63.12
Phenoxyethanol & parabens	0.80
Propylene glycol	3.00
Carbomer (Carbopol 981)	0.20
NaOH (10%)	0.33
Scleroglucan	1.00
Micropigment from Example 2	3.00
Titanium dioxide	3.00

Example 28: O/W Emulsion

	%
Methyl glucose sesquistearate	2.50
Tricontanyl PVP	1.00
Tocopherol & ascorbyl palmitate & ascorbic acid & citric acid & PEG-8	0.05
Decyl oleate	4.00
Isopropyl palmitate	6.00
Caprylic/capric triglyceride	5.00
Glyceryl stearate	1.00
Cetearyl alcohol	1.00
2-[(2,4-Methoxy)-phenyl]-4,6-bis[(2-hydroxy-4-methoxy)-phenyl]-(1,3,5)-triazine	2.00
Octyl methoxycinnamate	5.00
Deionised water	63.12
Phenoxyethanol & parabens	0.80
Carbomer (Carbopol 981)	0.20
Glycerol	3.00
NaOH (10%)	0.33
Scleroglucan	1.00
Micropigment from Example 1	4.00

Example 29: Lip-care preparation

	%
Glycerol	10.00
PEG-45 & dodecyl glycerol copolymer	1.50
Quaternium-18 bentonite	2.00
Microcrystalline wax	2.00
Beeswax	2.00
Glyceryl stearate SE	53.00
Pentaerythritol stearate & caprate & caprylate adipate	4.00
Castor oil	4.00
Methylene bis-benzotriazolyl tetramethylbutylphenol	5.00
Micropigment Example 2	5.00
Titanium dioxide	5.00
Zinc oxide	5.00
Octyl methoxycinnamate	4.00
Eucerinum anhydricum	ad 100

Example 30: W/O Emulsion

	%
PEG-30 dipolyhydroxystearate	2.00
Isostearyl alcohol	20.00
Isostearic acid	10.00
Octyl triazone	3.00
Deionised water	58.75
Glycerol	5.00
Methylparaben	0.17
Propylparaben	0.03
MgSO ₄ ·7H ₂ O	0.75
Micropigment from Example 2	4.00

Example 31: O/W Emulsion

		<u>%</u>
A	Polyglyceryl-3 methylglucose distearate	2.0
	Decyl oleate	5.7
	Isopropyl palmitate	5.0
	Caprylic/capric triglyceride	6.5
	Octyl methoxycinnamate	5.0
B	Glycerol	3.0
	Phenonip	0.5
	Deion. water	62.9
C	Carbomer 141	0.2
	Isopropyl palmitate	0.8
D	50% Suspension from Example 8	8.0
E	NaOH (10%)	as required

Example 32: O/W Emulsion

		<u>%</u>
A	Polyglyceryl-3 methylglucose distearate	2.0
	Decyl oleate	5.7
	Isopropyl palmitate	5.0
	Caprylic/capric triglyceride	6.5
B	Glycerol	3.0
	Phenonip	0.5
	Deion. water	62.9
C	Carbomer 141	0.2
	Isopropyl palmitate	0.8
D	Suspension from Example 2	6.0
E	NaOH (10%)	as required

Example 33: (O/W Emulsion)

	%
A Polyglyceryl-3 methylglucose distearate	2.0
Decyl oleate	5.7
Isopropyl palmitate	5.0
Caprylic/capric triglyceride	6.5
Octyl triazone	2.0
B Glycerol	3.0
Phenonip	0.5
Water	62.3
C Carbomer 141	0.2
Isopropyl Palmitate	0.8
D 2,2'-Methylene bis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol micropigment suspension (50%)	8.0
Octyl triazone micropigment suspension (50%)	4.0
E NaOH (10%)	as required

Example 34: O/W Emulsion

	%
A Polyglyceryl-3 methylglucose distearate	2.0
Decyl oleate	5.7
Isopropyl palmitate	5.0
Octyl triazone	2.0
Caprylic/capric triglyceride	6.5
B Glycerol	3.0
Phenonip	0.5
Water	68.3
C Carbomer 141	0.2
Isopropyl palmitate	0.8
D Micropigment from Example 2	6.0
E NaOH (10%)	as required

Example 35: W/O Emulsion

	%
PEG-30 dipolyhydroxystearate (Arlacel P 135 [®])	3.00
PEG-22/ dodecyl glycol copolymer (Elfacos ST 37 [®])	1.00
Microcrystalline wax	1.00
Hydrogenated castor oil	0.50
Magnesium stearate	1.00
Octyl stearate	15.00
Coco glycerides	2.00
Mineral oil	3.00
Phenoxyethanol & parabens	1.00
Octyl methoxycinnamate	5.00
Dimethicone	0.10
Water	54.40
Magnesium sulfate ($MgSO_4 \times 7 H_2O$)	1.00
Propylene glycol	4.00
50% Suspension from Example 3	8.00

Example 36: W/O Emulsion

	%
Methoxy PEG-22/dodecyl glycol copolymer (Elfacos E 200 [®])	3.00
PEG-22/ dodecyl glycol copolymer (Elfacos ST 37 [®])	3.00
Hydroxyoctacosanyl hydroxystearate (Elfacos C 26 [®])	3.00
Octyl stearate	15.00
Coco glycerides	2.00
Mineral oil	3.00
Phenoxyethanol & parabens	1.00
4-Methylbenzylidene camphor	3.00
Dioctyl butamidotriazone	3.00
Dimethicone	0.20
Water	53.00
Phenylbenzimidazole sulfonic acid	3.00
Magnesium sulfate ($MgSO_4 \times 7 H_2O$)	0.80
Propylene glycol	4.00
Micropigment from Example 5	3.00

Example 37: W/O Emulsion

	%
Polyglyceryl-2 dipolyhydroxystearate (Dehymuls PGPH®)	2.00
PEG-30 dipolyhydroxystearate (Arlacel P 135®)	2.00
Hydroxyoctacosanyl hydroxystearate (Elfacos C 26®)	2.00
Zinc stearate	1.00
Octyl stearate	15.00
Coco glycerides	2.00
Mineral oil	3.00
Phenoxyethanol & parabens	1.00
2,4-Bis[[4-(2-ethyl-hexyloxy)-2-hydroxy]-phenyl]-6-(4-methoxy-phenyl)-1,3,5-triazine	2.00
Octyl salicylate	3.00
Dimethicone	0.20
Water	56.70
Magnesium sulfate ($\text{MgSO}_4 \times 7 \text{ H}_2\text{O}$)	1.00
Propylene glycol	4.00
Micropigment from Example 6	5.00

Example 38: W/O Emulsion

	%
Polyglyceryl-2-dipolyhydroxystearate (Dehymuls PGPH®)	3.00
Glyceryl oleate (Monomuls 90-O 18®)	1.00
Caprylic / capric triglyceride	6.00
Octyldodecanol	6.00
Cetearyl isononanoate	5.00
Tocopheryl acetate	1.00
Cera alba	1.20
Glycerol (86 %)	5.00
Phenonip	0.50
Octyl methoxycinnamate	4.00
Octyl triazone	3.00
Micropigment from Example 3	5.00
Water	ad 100

Example 39: W/O Emulsion

	%
Polyglyceryl-2-dipolyhydroxystearate (Dehymuls PGPH®)	3.00
Glyceryl oleate (Monomuls 90-O 18®)	1.00
Caprylic / capric triglyceride	6.00
Octyldodecanol	6.00
Cetearyl isononanoate	5.00
Octyl methoxycinnamate	3.00
Tocopheryl acetate	1.00
Cera alba	1.20
Glycerol (86 %)	5.00
Phenonip	0.50
Micropigment from Example 10	5.00
Water	ad 100

Example 40: O/W Emulsion

	%
Tego Care CG 90 (Goldschmidt AG)	6.00
Cetearyl alcohol	1.50
Glyceryl stearate	0.50
Octyldodecanol	7.00
Capric/caprylic triglyceride	5.00
Cetearyl isononanoate	6.00
Octyl methoxycinnamate	3.00
Deionised water	51.14
Carbomer	0.20
NaOH (45%)	1.13
Glycerol	5.00
Methylparaben	0.17
Propylparaben	0.03
Terephthalidene-dibornanesulfonic acid	1.50
Micropigment from Example 5 (50% suspension)	12.00

Example 41: O/W Microemulsion

	%
Cetareth-12	8.0
Cetearyl alcohol	4.0
Cetearyl isononanoate	20.0
Butyl methoxydibenzoylmethane	2.0
Deionised water	ad 100.0
Carbomer	0.2
Preservative	as required
Magnesium sulfate ($\text{MgSO}_4 \times 7 \text{ H}_2\text{O}$)	3.0
Micropigment from Example 9 (50% suspension)	8.0

Example 42: O/W/O Emulsion

	%
Polyglyceryl-2-polyhydroxystearate	5.0
Mineral oil	12.5
Stearic acid	2.0
Cetearyl isononanoate	12.5
Methylbenzylidene camphor	2.0
Homosalate	2.0
Deionised water	ad 100.0
Carbomer	0.2
Preservative	as required
NaOH	as required
Micropigment from Example 2 (50% suspension)	8.0

Example 43: O/W Emulsion

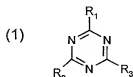
	%
Glycerol stearate/polyethylene glycol (MW100) stearate	3.0
Cetyl/stearyl alcohol-20EO (Eumulgin B 2)	1.0
Cetyl/stearyl alcohol (Lanette O)	2.0
Caprylic/capric triglyceride (Myritol 318)	4.0
Dicaprylic ether	6.0
Mineral oil and Quaternium-18 hectorite	3.0
Glycerol stearate, cetyl/stearyl alcohol, cetyl palmitate, coco glyceride (Cutina CBS)	2.0
4-Methylbenzylidene camphor	1.0
Octyl triazone	2.0
Deionised water	ad 100.0
Glycerol, 85%	3.0
Preservative	as required
Magnesium aluminium silicate (Vegum Ultra)	0.3
NaOH	as required
Micropigment from Example 2 (50% suspension)	10.0

Patent claims:

1. Use of a mixture of micronised organic UV filters in protecting human and animal skin and hair against the damaging effect of UV radiation.

2. Use according to claim 1, wherein the organic UV filters are selected from triazine or benzotriazole derivatives, amides containing a vinyl group, cinnamic acid derivatives, sulfonated benzimidazoles, Fischer base derivatives, diphenylmalonic acid dinitriles, oxalyl amides, camphor derivatives, diphenyl acrylates, para-aminobenzoic acid (PABA) and derivatives thereof, salicylates and benzophenones.

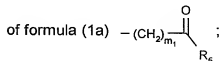
3. Use according to claim 1 or 2, wherein the organic UV filters are selected from triazine derivatives of formula



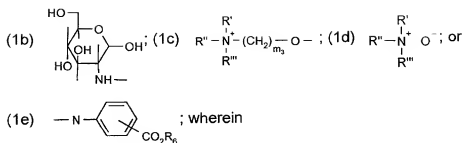
wherein

R_1 , R_2 and R_3 are each independently of the others hydrogen; OH; C_1 - C_{18} alkoxy; $-NH_2$; $-NH-R_4$; $-N(R_4)_2$; $-OR_4$,

R_4 is C_1 - C_8 alkyl; phenyl; phenoxy; anilino; pyrrolo, wherein phenyl, phenoxy, anilino and pyrrolo are unsubstituted or may be substituted by one, two or three OH groups, carboxy, $-CO-NH_2$, C_1 - C_8 alkyl or C_1 - C_8 alkoxy; a methyldene-camphor group; a group of formula $-(CH=CH)_mC(=O)-OR_4$; a group of formula $\text{---} \text{C}_6\text{H}_4 \text{---} CH=CH-C(=O)-OH$ or a corresponding alkali metal, ammonium, mono-, di- or tri- C_1 - C_4 alkylammonium, mono-, di- or tri- C_2 - C_4 alkanolammonium salt, or a C_1 - C_3 alkyl ester thereof; or a radical



R_5 is hydrogen; C_1 - C_8 alkyl unsubstituted or substituted by one or more OH groups; C_1 - C_8 alkoxy; amino; mono- or di- C_1 - C_8 alkylamino; M; a radical of formula



R' , R'' and R''' are each independently of the others C_1 - C_{14} alkyl unsubstituted or substituted by one or more OH groups;

R_6 is hydrogen; M ; C_1 - C_5 alkyl; or a radical of formula $-(\text{CH}_2)_{m_2}-\text{O}-\text{T}_1$;

M is a metal cation;

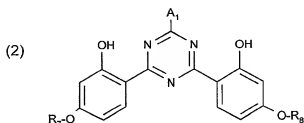
T_1 is hydrogen; or C_1 - C_8 alkyl;

m is 0 or 1;

m_2 is from 1 to 4; and

m_3 is from 2 to 14.

4. Use according to claim 1 or 2, wherein the organic UV filters are selected from triazine derivatives of formula



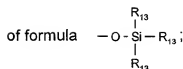
wherein

R_7 and R_8 are each independently of the other C_1 - C_{18} alkyl; C_2 - C_{18} alkenyl; a radical of formula $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-\text{T}_1$; or

R_7 and R_8 are a radical of formula (2a) $R_9-\left[\overset{R_{10}}{\underset{R_{11}}{\text{Si}}}-\text{O}-\overset{R_{10}}{\underset{R_{11}}{\text{Si}}}-\text{R}_{12}\right]_{p_1}$;

R_9 is a direct bond; a straight-chain or branched C_1 - C_4 alkylene radical or a radical of formula $-\text{C}_{m_1}\text{H}_{2m_1}-\text{O}-$;

R_{10} , R_{11} and R_{12} are each independently of the others C_1 - C_{18} alkyl; C_1 - C_{18} alkoxy or a radical

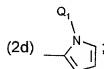
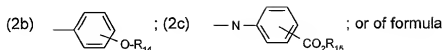


R_{13} is C_1 - C_5 alkyl;

m_1 is from 1 to 4;

p_1 is from 0 to 5;

A_1 is a radical of formula



R_{14} is hydrogen; C_1 - C_{10} alkyl, $-(CH_2CHR_{16}-O)_{n_1}-R_{15}$; or a radical of formula



R_{15} is hydrogen; M; C_1 - C_5 alkyl; or a radical of formula $-(CH_2)_{m_2}-O-(CH_2)_{m_3}-T_1$;

R_{16} is hydrogen; or methyl;

T_1 is hydrogen; or C_1 - C_8 alkyl;

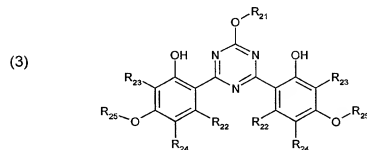
Q_1 is C_1 - C_{18} alkyl;

M is a metal cation;

m_2 and m_3 are each independently of the other from 1 to 4; and

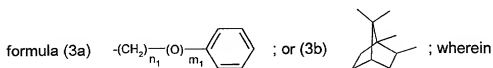
n_1 is from 1 to 16.

5. Use according to claim 1 or 2, wherein the organic UV filters are selected from triazine derivatives of formula



wherein

R_{21} is C_1 - C_{30} alkyl; C_2 - C_{30} alkenyl; C_5 - C_{12} cycloalkyl unsubstituted or mono- or poly-substituted by C_1 - C_5 alkyl; C_1 - C_5 alkoxy- C_1 - C_{12} alkyl; amino- C_1 - C_{12} alkyl; C_1 - C_5 -monoalkylamino- C_1 - C_{12} alkyl; C_1 - C_5 dialkylamino- C_1 - C_{12} alkyl; a radical of



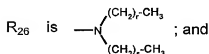
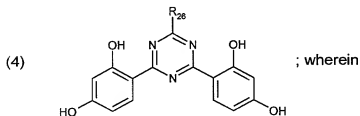
R_{22} , R_{23} and R_{24} are each independently of the others hydrogen, -OH; C_1 - C_{30} alkyl, C_2 - C_{30} alkenyl,

R_{25} is hydrogen; or C_1 - C_5 alkyl;

m_1 is 0 or 1; and

n_1 is from 1 to 5.

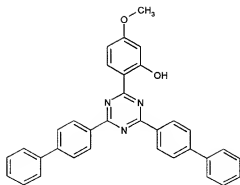
6. Use according to claim 1 or 2, wherein the organic UV filters are selected from triazine derivatives of formula



r and s are each independently of the other from 0 to 20.

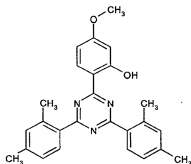
7. Use according to claim 1 or 2, wherein the organic UV filters are selected from triazine derivatives of formula

(20a)



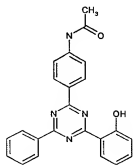
8. Use according to claim 1 or 2, wherein the organic UV filters are selected from triazine derivatives of formula

(24a)

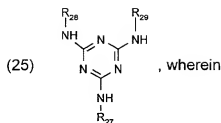


9. Use according to claim 1 or 2, wherein the organic UV filters are selected from triazine derivatives of formula

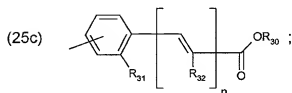
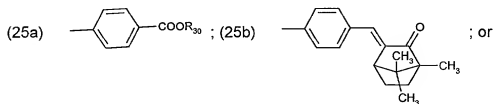
(24b)



10. Use according to claim 1 or 2, wherein the organic UV filters are selected from triazine derivatives of formula



R_{27} , R_{28} and R_{29} are each independently of the others a radical of formula



R_{30} is hydrogen; an alkali metal; an ammonium group $-N(R_{33})_4$,

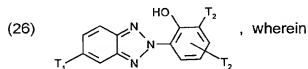
R_{33} is hydrogen, C_1 - C_5 alkyl; or a polyoxyethylene radical that has from 1 to 10 ethylene oxide units and the terminal OH group can be etherified with a C_1 - C_5 alcohol;

R_{31} is hydrogen; -OH; or C_1 - C_6 alkoxy;

R_{32} is hydrogen or $-COOR_{30}$; and

n is 0 or 1.

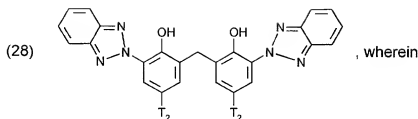
11. Use according to either claim 1 or claim 2, wherein the organic UV filters are selected from benzotriazole derivatives of formula



T_1 is C_1 - C_5 alkyl or hydrogen; and

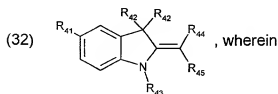
T_2 is C_1 - C_5 alkyl or phenyl-substituted C_1 - C_5 alkyl.

12. Use according to either claim 1 or claim 2, wherein the organic UV filters are selected from benzotriazole derivatives of formula



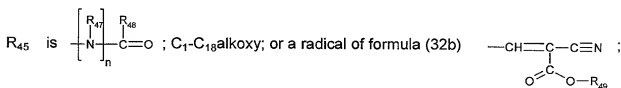
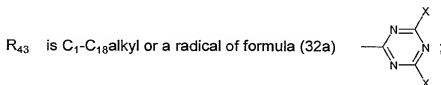
T_2 is C_1 - C_4 alkyl or phenyl-substituted C_1 - C_5 alkyl.

13. Use according to either claim 1 or claim 2, wherein the Fischer base aldehydes correspond to formula



R_{41} is hydrogen; C_1 - C_5 alkyl; C_1 - C_{18} alkoxy; or halogen;

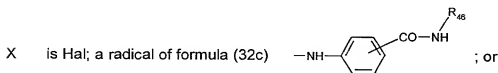
R_{42} is C_1 - C_8 alkyl; C_5 - C_7 cycloalkyl; or C_6 - C_{10} aryl;

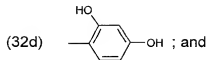


R_{46} and R_{47} are each independently of the other hydrogen; or C_1 - C_5 alkyl;

R_{48} is hydrogen; C_1 - C_5 alkyl; C_5 - C_7 cycloalkyl; phenyl; phenyl- C_1 - C_3 alkyl;

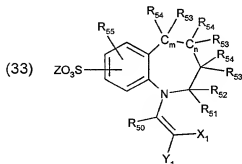
R_{49} is C_1 - C_{18} alkyl;





n is 0; or 1.

14. Use according to claim 1 or 2, wherein the organic UV filters are selected from compounds of formula



wherein

R_{50} , R_{51} , R_{52} , R_{53} , R_{54} are each independently of the others hydrogen, C_1 - C_8 alkyl or C_5 - C_{10} -cycloalkyl;

R_{55} is hydrogen; C_1 - C_8 alkyl; C_5 - C_{10} cycloalkyl; hydroxy; C_1 - C_8 alkoxy; $COOR_{56}$; or $CONR_{57}R_{58}$;

R_{56} , R_{57} and R_{58} are each independently of the others hydrogen or C_1 - C_6 alkyl;

X and Y are each independently of the other hydrogen, $-CN$; CO_2R_{59} ; $CONR_{59}R_{60}$; or COR_{59} ; it being possible for the radicals X and Y additionally to be a C_1 - C_8 alkyl radical, a C_5 - C_{10} alkyl radical or a heteroaryl radical having 5 or 6 ring atoms, it also being possible for X and Y or

R_{50} together with one of the radicals X and Y to be the radical for completing a 5- to 7-membered ring which may contain up to 3 hetero atoms, it being possible for the ring atoms to be substituted by exocyclic double-bonded oxygen and/or by C_1 - C_8 alkyl and/or by C_5 - C_{10} cycloalkyl radicals and/or to contain C=C double bonds;

Z is hydrogen; ammonium; an alkali metal ion; or the cation of an organic nitrogen base used for neutralisation of the free acid group,

R_{59} and R_{60} are each independently of the other hydrogen, C_1 - C_8 alkyl or C_5 - C_{10} cycloalkyl; and

n and m are each independently of the other 0 or 1.

15. A process for the preparation of mixtures of the organic UV filters suitable for use according to the invention defined in any one of claims 1 to 14, wherein the UV filters, which are in micronised form, are intimately mixed together.

16. A process for the preparation of mixtures of the organic UV filters suitable for use according to the invention defined in any one of claims 1 to 14, wherein the organic UV filters are micronised in the form of mixtures of at least two single substances.

17. A process for the preparation of mixtures of the organic UV filters suitable for use according to the invention defined in any one of claims 1 to 14, wherein at least two single substances are melted together, the melt is cooled and the resulting composite is then subjected to a micronisation process.

18. A composite, obtainable by melting together at least two of the organic UV filters defined in any one of claims 1 to 14.

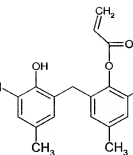
19. Use according to any one of claims 1 to 14, wherein an inorganic pigment is additionally incorporated into the mixture.

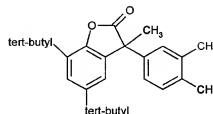
20. Use according to claim 19, wherein the inorganic pigments are selected from TiO_2 , ZnO , iron oxides, mica and titanium or zinc salts of organic acids.

21. A composite, obtainable by melting together at least two of the organic UV filters defined in any one of claims 1 to 14 and at least one of the inorganic pigments defined in claim 19 or 20.

22. Use according to any one of claims 1 to 14, wherein an antioxidant is additionally incorporated into the mixture.

23. Use according to claim 22, wherein the antioxidant is selected from tocopherols, ellagic acid, propyl gallate, butylated hydroxytoluene, butylated hydroxyanisole, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)mesitylene, tetrakis[methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)-

propionate]methane, the compound of formula , the

compound of formula , vanillin, ubiquinone, ferulic acid,

ferulic acid derivatives, rutinic acid, rutinic acid derivatives; urocanic acid, urocanic acid derivatives; and propolis.

24. A composite, obtainable by melting together at least two of the organic UV filters defined in any one of claims 1 to 14 and at least one of the antioxidants defined in claim 22 or 23 and optionally one or more inorganic pigments.

25. Use according to any one of claims 1 to 14, wherein a cationic or anionic compound is incorporated into the mixture.

26. Use according to claim 24, wherein the cationic or anionic compound is selected from camphor benzalkonium methosulfates, fatty amines, betaines, quats, citric acid mono-glyceride, sodium methylcocoyl taurate, phospholipids, ceramides and phytosterols.

27. A composite, obtainable by melting together at least two of the organic UV filters defined in any one of claims 1 to 14 and at least one of the cationic or anionic compounds defined in claims 25 and 26.

28. Use according to any one of claims 1 to 14, wherein a pharmaceutical or cosmetic active ingredient is additionally incorporated into the mixture.

29. A cosmetic formulation, comprising a mixture of at least two of the organic UV filters

defined in any one of claims 1 to 14, optionally one or more antioxidants and/or inorganic pigments and/or a cationic or anionic compound, and also cosmetically acceptable carriers or adjuvants.

30. A cosmetic formulation according to claim 29, which additionally comprises an oil-soluble, non-micronised UV filter.

31. A pharmaceutical formulation, comprising a mixture of at least two of the organic UV filters defined in any one of claims 1 to 14, optionally one or more antioxidants and/or inorganic pigments and/or a cationic or anionic compound, and also pharmaceutically acceptable carriers or adjuvants.

DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATIONS

☒ Original ☐ Supplemental ☐ Substitute ☒ PCT

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if more than one name is listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

MICROPIGMENT MIXTURE

which is described and claimed in:

☐ the attached specification.
☐ the specification in U.S. Application No. _____
 filed _____, and as amended on _____ (if applicable).
 (day/month/year) (day/month/year)

☒ the specification in International Application No. **PCT/EP 00/05314**
 filed **08/06/00**
 (day/month/year)
 assigned U.S. Application No. _____ (if applicable), and as amended
☐ under PCT Article 19 on _____ (if applicable)
 (day/month/year)
☐ under PCT Article 34 on _____ (if applicable)
 (day/month/year)
☐ and further amended on _____ (if applicable)
 (day/month/year)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information which is known by me to be material to the patentability of this application as defined in 37 C.F.R. § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119 (a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America relating to this subject matter having a filing date before that of the application on which priority is claimed:

COUNTRY/REGION
(OR PCT)

APPLICATION No.

FILING DATE
(day/month/year)

PRIORITY CLAIMED

Europe
(designating DE)

99810543.1

18/06/99

☒ Yes ☐ No

☐ Yes ☐ No

☐ Yes ☐ No

☐ Yes ☐ No

☐ Yes ☐ No

I hereby claim the benefit under 35 U.S.C. § 119 (e) of any United States provisional application(s) listed below:

APPLICATION NO.

FILING DATE
(day/month/year)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s) or PCT international application(s) designating the United States listed below and, insofar as the application discloses and claims subject matter in addition to that disclosed in the prior copending application, I acknowledge the duty to disclose all information known by me to be material to patentability as defined in 37 C.F.R. § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. APPLICATION
No.

FILING DATE
(day/month/year)

STATUS

☐ Patented ☐ Pending ☐ Abandoned

☐ Patented ☐ Pending ☐ Abandoned

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PCT APPLICATION
No.
(designating the U.S.)

INTERNATIONAL
FILING DATE
(day/month/year)

U.S. APPLICATION
No.
(if any)

STATUS

☐ Patented

☐ Pending

☐ Abandoned

I hereby appoint the following attorneys and agents, associated with Customer No. 000324, each of them with full power of substitution, revocation and appointment of associates, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole
or first joint inventor Helmut LUTHER

Inventor's signature Helmut Luther Date 7/11/2007
(day/month/year)

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